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## Volume 2. The Aqueous-Phase Chemistry

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# CHEMICAL TRANSFORMATION MODULES FOR EULERIAN ACID DEPOSITION MODELS

## Volume II. The Aqueous-Phase Chemistry

by

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This study focuses on the review and evaluation of mechanistic and kinetic data for aqueous-phase reactions that lead to the production of acidic substances in the environment. The intent of this research is to provide a framework that can be used to develop a state-of-the-art aqueous-phase mechanism for use in the Regional Acid Deposition Model under development at NCAR. In the research effort described in this report, thirty-one tables of kinetic data and twenty-seven tables of thermodynamic data were compiled and evaluated. A set of recommended rate expressions and kinetic data were then prepared for the predominant aqueous-phase pathways leading to acid generation in the troposphere.

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# ABSTRACT

The objective of this research effort was to develop a comprehensive mechanism for the aqueous-phase chemistry of atmospheric water droplets that considered all the potentially relevant chemical reactions. Reactions have been subdivided into reversible and irreversible categories. Reversible reactions are quantitatively described in terms of the appropriate mass action expressions, stoichiometric coefficients, equilibrium constants, and reaction enthalpies. Irreversible reactions are described likewise in terms of their stoichiometries, empirical rate laws or, in specific cases, fundamental rate expressions, rate constants, and activation parameters.

The kinetically-controlled irreversible reactions were initially compiled from the previously reported treatments of Jacob and Hoffmann (1983), Hoffmann and Jacob (1984), Chameides and Davis (1982), Graedel and Goldberg (1983), and Chameides (1984). These compilations were then expanded extensively by drawing upon other kinetic compilations such as those by Farhataziz and Ross (1977), Ross and Neta (1979), and Dorfman and Adams (1973). In addition to these existing compendia, the current literature was used extensively to provide a relatively complete list of potentially important kinetic systems. When appropriate multiple sets of reported kinetic data for specific reactions have been reevaluated in terms of self-consistent rate expressions, rate constants, and activation parameters.

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# CHAPTER I

# INTRODUCTION

## A. GOALS

The goal of this research was to review and evaluate mechanistic and rate constant data for aqueous-phase reactions that lead to the production of acidic substances in the environment. The intent of this effort is to provide an advanced framework that can be used to develop an advanced aqueous-phase mechanism for use in the Regional Acid Deposition Model under development at NCAR. Previous efforts in this laboratory established the basic framework for the development of a model for the detailed chemistry of clouds and fogs (Jacob and Hoffmann, 1983). Additional work by Chameides and Davis (1982), Chameides (1984), Seigneur and Saxena (1984), and Graedel and Goldberg (1983) has been used as a basis for improvement of our initial modeling efforts.

The original model developed by Jacob and Hoffmann (1983) was a hybrid kinetic and equilibrium model. A basic set of 32 equilibria involving important species found in fog and cloud water were considered (Munger et al., 1983). Superimposed on this basis-set of equilibria were an additional set of seven empirical rate equations for the time-dependent aqueous-phase oxidation of S(IV) and N(III) to produce $H^+$, S(VI), and N(V). At each time step in the numerical computation, the complete equilibrium problem was solved for reactions that had characteristic times much shorter than the size of the time step. In addition to the purely chemical pathways, the physical processes of nucleation scavenging, droplet growth on condensation nuclei, and gas-liquid mass transfer were considered. Jacob and Hoffmann (1983) found that the important oxidants of S(IV) were $O_2$ as catalyzed by

Fe(III) and Mn(II), $H_2O_2$, and $O_3$. Nitrate production was found to be dominated by $HNO_3$ gas-phase scavenging. Gas-phase ammonia and hydrogen peroxide were also scavenged efficiently. Formation of hydroxyalkylsulfonates, due to the in situ reaction of aldehydes and S(IV), was found to significantly increase the droplet capacity for S(IV) but did not slow down the net S(IV) oxidation rate leading to cloud acidification. The concentrations of major aqueous-phase species were found to be controlled primarily by condensation, evaporation, and pH. The composition of the precursor haze aerosol or cloud condensation nuclei will determine to a large extent the observed chemical speciation of the droplet phase. Hoffmann and Jacob (1984) have considered a variation of the above model that incorporates dynamic gas-phase chemistry in addition to the aqueous-phase module. Chameides and Davis (1982) and Chameides (1984) have incorporated coupled gas- and aqueous phase photochemistry into the development of a model for the acidification of remote marine stratiform clouds. They have shown that, in addition to the above pathways, aqueous-phase free radical pathways can contribute substantially to the generation of acidity via the in situ oxidation of S(IV) and HCHO to S(VI) and formic acid, respectively. The principal oxidants of S(IV) as identified by Chameides were $H_2O_2$, $O_3$, OH, and $HO_2$. Parameters found to affect the S(IV) to S(VI) conversion rate were the accommodation coefficient for the reactive species of interest, the liquid water content, and the ambient levels of $SO_2$ and $HNO_3$. Similar considerations in model development were made by Graedel and Goldberg (1983). Seigneur and Saxena (1984) have adapted the Jacob and Hoffmann (1983) approach in a coupled gas-phase and aqueous-phase kinetic model. Their results were in general agreement with Jacob and Hoffmann for the special cases of urban fogs and clouds. The main effect of the addition of the gas-phase module was to provide dynamic non-aqueous sources of $HNO_3$ and to illustrate that the gas-phase hydrocarbon chemistry will dominate OH chemistry (i.e., aqueous-phase OH chemistry due to radical scavenging appears to be inconsequential).

An extensive review of the literature through 1982 and a detailed compilation of the associated kinetic expressions pertaining to the aqueous-phase pathways for the production of acidity, S(VI), and N(V) has also been made by Hoffmann and Jacob (1984). The work described in that article was supported by the U.S. E.P.A. The article forms the basis for the development of a more extensive list of fundamental kinetic and thermodynamic relationships.

## B. APPROACH AND METHODS EMPLOYED

The underlying philosophy of the research effort conducted in this study is to treat all possible chemical reactions that may be relevant to aqueous-phase cloud chemistry. Reactions are subdivided into reversible and irreversible categories. Reversible reactions are quantitatively described in terms of the appropriate mass action expressions, stoichiometric coefficients, equilibrium constants, and reaction enthalpies. Irreversible reactions are described likewise in terms of their stoichiometries, empirical rate law or, in some special cases, fundamental rate expression, rate constants, and activation parameters.

The kinetically-controlled irreversible reactions were initially compiled from the previously reported treatments of Jacob and Hoffmann (1983), Hoffmann and Jacob (1984), Chameides and Davis (1982), Graedel and Goldberg (1983), and Chameides (1984). These compilations were then expanded extensively by drawing upon other kinetic compilations such as those by Farhataziz and Ross (1977), Ross and Neta (1979), and Dorfman and Adams (1973). In addition to these existing compendia, the current literature was used extensively to provide a relatively complete list of potentially important kinetic systems. Twenty-five tables of free radical reactions (Tables K1 - K25 of Appendix A) were compiled for this report. The majority of these tables focus on hydroxyl radical as a principal oxidant. In addition to its reaction with aquated sulfur dioxide, OH may react competitively with a wide variety of other organic and inorganic species in aqueous solution. We believe that consideration of OH reactions with a select few inorganic and organic constituents may not adequately reflect reality as in the case of complicated gas-phase mechanisms involving OH. Hydroxyl radical is highly reactive. Its competitive reactions must be considered when an attempt is made to ascertain its role with respect to S(IV) oxidation. Similar considerations are necessary for the other highly reactive oxidants such as hydrogen peroxide and ozone. In many cases, a number of rate constants for the same radical reaction have been reported because of an apparent variation with pH as observed by different investigators.

In the case of ozone, hydrogen peroxide, and metal-catalyzed autoxidation, detailed tables of comparative kinetic data were compiled. Empirical rate laws reported by the various investigators and the conditions over which they are applicable are given. When appropriate, the kinetic data of the most relevant studies are recast in terms of self-consistent rate laws, rate constants, and activation parameters.

In these particular cases, recommended intrinsic rate expressions and rate constants are given.

Thermodynamic data (Tables T1 - T27) on a number of reactions of interest were compiled in a fashion similar to the kinetic data set. Values for gas & liquid, metal & ligand, acid & base, precipitation & dissolution, and aldehyde & adduct equilibria are treated in great detail. If the thermodynamic data is needed to solve problems defined by the kinetic equations of Tables K1 - K31, it is included in the thermodynamic data base. Much of the thermodynamic data has already been critically evaluated by Smith and Martell (1976) and Martell and Smith (1977). We have indicated in the tables our recommended values for the thermodynamic data when more than one data set is available for identical reactions and conditions. Enthalpy values have been included in this compendium. Of course, these values are essential for variable temperature calculations.

# CHAPTER II

# COMPARISON OF S(IV)-OXIDANT SYSTEMS

## A. INTRODUCTION

The thermodynamic and kinetic data compiled in this study are presented in Tables T1 to T27 and K1 to K31 of Appendix A and B (see Appendix A for the kinetic data and Appendix B for the thermodynamic data). After these data were compiled, the major kinetic pathways for in situ sulfate production from S(IV) oxidation were examined comparatively. Many of the important pathways have been identified previously by Hoffmann and Jacob (1984) and by others such as Chameides (1984), Graedel and Goldberg (1983), Jacob and Hoffmann (1983), and Martin (1984). As noted before, in situ pathways for the production of nitric acid are relatively minor contributors to nitrate accumulation in the droplet phase because of the low Henry's Law constants for $NO_2$ and NO (see Table T2) and because of second-order reaction kinetics with respect to $[NO_2]$ (Schwartz and Lee, 1983; Schwartz, 1984). The predominant pathways for S(IV) transformation involve reactions with $H_2O_2$, $O_3$, $O_2$ ($Fe^{3+}$ and $Mn^{2+}$ catalyzed), OH, HONO, $CH_3OOH$, $CH_3CO_3H$, PAN, $HO_2$, HCHO, and soot. A summary of recommended rate expressions and kinetic data for these reactions is given in Table 1.

## TABLE 1

## RECOMMENDED KINETIC DATA FOR THE S(IV)-OXIDANT SYSTEM

| | | | |
|---|---|---|---|
| $H(SO_2)$ | 1.24E+00 (M/atm) | $pK_1$ = | 1.89 |
| $H(O_3)$ | 1.00E-02 (M/atm) | $pK_2$ = | 7.22 |
| $H(H_2O_2)$ | 1.60E+05 (M/atm) | T(oC) = | 25.00 |
| H(OH) | 2.00E+02 (M/atm) | pH = | 5.00 |
| $P(O_3)$ | 5.00E-08 (atm) | $[H^+]$ = | 1.00E-05 |
| $P(H_2O_2)$ | 1.00E-09 (atm) | $K_{a1}$ = | 1.29E-02 |
| P(OH) | 1.00E-13 (atm) | $K_{a2}$ = | 6.03E-08 |
| $P(SO_2)$ | 2.00E-08 (atm) | DEN = | 1.30E-07 |
| a0 = | 7.71E-04 | $[O_3]$ = | 5.00E-10 $[O_3] = H(O_3)P(O_3)$ |
| a1 = | 9.93E-01 | [S(IV)] = | 3.22E-05 [S(IV)] = $H(SO_2)P(SO_2)/a0$ |
| a2 = | 5.98E-03 | $[SO_2]$ = | 2.00E+01 ppb |

| SPECIES | [C](atm) | H(M/atm) | [C](M) |
|---|---|---|---|
| HONO | 1.00E-09 | 4.90E+01 | 4.90E-08 |
| $CH_3OOH$ | 2.00E-10 | 1.00E+03 | 2.00E-07 |
| $CH_3COOOH$ | 1.00E-11 | 1.00E+04 | 1.00E-07 |
| PAN | 3.00E-08 | 3.60E+00 | 1.08E-07 |
| $HO_2$ | 4.00E-11 | 5.00E+04 | 2.00E-06 |
| HCHO | 3.00E-08 | 6.30E+03 | 1.89E-04 |

| OXIDANT | RATE LAW & CONSTANTS | R(M/S) | (mol/M3H) | (%/HR) |
|---|---|---|---|---|
| Ozone | $R=(k_0a_0) + k_1a_1 + k_2a_2)[O_3][S(IV)]$ | 1.50E-07 | 1.08E-07 | 1.31E+01 |
| | $k_0$ = 2.40E+-4 (1/Ms) | | | |
| | $k_1$ = 3.70E+05 (1/Ms) | | | |
| | $k_2$ = 1.50E+09 (1/Ms) | | | |
| | LWC = 0.20 ($g/m^3$) | | | |
| $H_2O_2$ | $R=k[H^+]]H_2O_2][S(IV)]_{a1}/(1+K[H^+])$ | 3.83E-06 | 2.76E-06 | 3.34E+02 |
| | k = 7.50E+07 (1/Ms) | | | |
| | K = 1.30E+01 (1/M) | | | |
| | LWC = 0.20 ($g/m^3$) | | | |
| OH | $R=(k_1a_1 + k_2a_2)[OH][S(IV)]$ | 6.09E-06 | 4.39E-06 | 5.31E+02 |
| | $k_1$ = 9.50E+09 | | | |
| | $k_2$ = 5.50E+09 | | | |
| | LWC = 0.20 ($g/m^3$) | | | |

| | RATE LAWS | EVALUATED RATES & CONSTANTS |
|---|---|---|
| HONO | $R= k[H^+][HSO^{3-}][NO^{2-}]$ | 4.21E-07 (M/s) |
| | k = 3.80E+03 | |
| | $[NO^{2-}] = a_1H(HONO)P(HONO)/a_0$ | 3.47E-06 (M) |
| | $a1 = K_{a1}/([H^+] + K_{a1})$ | 9.86E-01 |
| | $a0 = [H^+]/([H^+] + K_{a1})$ | 1.39E-02 |
| | $K_{a1}$ = 7.08E-04 (M) | |
| $CH_3OOH$ | $R=k[H^+][CH_3OOH][S(IV)]a_1$ | 1.12E-09 (M/s) |
| | k = 1.75E+07 ($1/M_2s$) | |

## COMPARISON OF S(IV)-OXIDANT SYSTEMS

| | | |
|---|---|---|
| $CH_3CO_3H$ | $R = (k_3[H^+] + k_2)[HSO_3^-][CH_3CO_3H]$ | 3.08E-09 (M/s) |
| | $k_3$ = 3.64E+07 ($1/M^2s$) | |
| | $k_2$ = 6.01E+02 (1/Ms) | |
| PAN | $R = k[PAN][S(IV)]a_2$ | 2.29E-09 (M/s) |
| | k = 1.01E+05 (1/Ms) | |
| $Fe/O_2$ | $R = k[Fe(III)][S(IV)]a_2$ | 2.31E-06 (M/s) |
| | k = 1.20E+06 (1/Ms) | |
| | [Fe(III)] = 1.00E-05 (M) | |
| $Mn/O_2$ | $R = k_2[Mn(II)][S(IV)]a_1 + k_1K_1[Mn]_2$ | 1.09E-06 (M/s) |
| | $k_2$ = 3.40E+-3 (1/Ms) | |
| | $k_1$ = 2.00E+09 (1/Ms) | |
| | $K_1$ = 1.26E-10 | |
| | [Mn(II)] = 1.00E-05 (M) | |
| Soot | $R = k_1K_1[C_x][S(IV)]^2/A$ | 1.44E-13 (M/s) |
| | $A = 1+K_2[S(IV)]+K_1[S(IV)]^2$ | 1.10E+01 |
| | $k_1$ = 1.04E-07 ($mol/g^{-s}$) | |
| | $K_1$ = 4.92E+-8 ($1/M^2$) | |
| | $K_2$ = 2.96E+05 (1/M) | |
| | $[C_x]$ = 3.00E-05 ($g/m^3$) | |
| | LWC = 2.00E-01 ($g/m^3$) | |
| | $[C_x]$ = 1.50E-01 (g/L) | |
| HCHO | $R = (k_1a_1+k_2a_2)K_d[S(IV)][HCHO]_T/(K_d+1)$ | 4.99E-07 (M/s) |
| | $k_1$ = 7.90E+0 (1/Ms) | |
| | $k_2$ = 2.48E+07 (1/Ms) | |
| | $K_d$ = 5.50E-04 | |

$HO_2$ $R = (k_1 a_{1b0} + k_2 a_{2b1})[S(IV)][HO_2]_T$ 2.27E-08 (1/Ms)

$k_1$ = 1.00E+06 (1/Ms)

$k_2$ = 1.00E+05 (1/Ms)

$K_a(HO_2)$ = 1.30E-05 (1/M)

$b_0$ = 4.35E-01

$b_1$ = 5.65E-01

| | RATE (M/s) | | | RATE (%/hr) | | |
|---|---|---|---|---|---|---|
| pH | $O_3$ | $H_2O_2$ | OH | $O_3$ | $H_2O_2$ | OH |
| 0.00 | 3.57E-13 | 2.74E-07 | 6.07E-11 | 3.13E-05 | 2.41E+01 | 5.33E-03 |
| 1.00 | 8.90E-13 | 1.67E-06 | 6.07E-10 | 7.82E-05 | 1.46E+02 | 5.33E-02 |
| 2.00 | 6.35E-12 | 3.39E-06 | 6.07E-09 | 5.58E-04 | 2.98E+02 | 5.33E-01 |
| 3.00 | 7.38E-11 | 3.78E-06 | 6.07E-08 | 6.49E-03 | 3.32E+02 | 5.33E+00 |
| 4.00 | 2.04E-09 | 3.83E-06 | 6.07E-07 | 1.79E-01 | 3.36E+02 | 5.33E+01 |
| 5.00 | 1.50E-07 | 3.83E-06 | 6.09E-06 | 1.31E+01 | 3.34E+02 | 5.31E+02 |
| 6.00 | 1.45E-05 | 3.83E-06 | 6.28E-05 | 1.18E+-3 | 3.11E+02 | 5.10E+03 |
| 7.00 | 1.44E-03 | 3.83E-06 | 8.19E-04 | 5.64E+04 | 1.50E+02 | 3.20E+04 |

Log Rate (M/s) Log Rate (%/hr)

COMPARISON OF S(IV)-OXIDANT SYSTEMS

| pH | $O_3$ | $H_2O_2$ | OH | $O_3$ | $H_2O_2$ | OH |
|---|---|---|---|---|---|---|
| 0.00 | -12.45 | - 6.56 | -10.22 | - 4.50 | 1.38 | - 2.27 |
| 1.00 | -12.05 | - 5.78 | - 9.22 | - 4.11 | 2.17 | - 1.27 |
| 2.00 | -11.20 | - 5.47 | - 8.22 | - 3.25 | 2.47 | - 0.27 |
| 3.00 | -10.13 | - 5.42 | - 7.22 | - 2.19 | 2.52 | 0.73 |
| 4.00 | - 8.69 | - 5.42 | - 6.22 | - 0.75 | 2.53 | 1.73 |
| 5.00 | - 6.82 | - 5.42 | - 5.22 | 1.12 | 2.52 | 2.73 |
| 6.00 | - 4.84 | - 5.42 | - 4.20 | 3.07 | 2.49 | 3.71 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 7.00 | - 2.84 | - 5.42 | - 3.09 | 4.75 | 2.18 | 4.50 |

---

Log Rate (M/s)

| pH | $H_2O_2$ | $CH_3OOH$ | $CH_3CO_3H$ | PAN | HONO | Fe(III) | Mn(II) |
|---|---|---|---|---|---|---|---|
| 0.00 | - 6.56 | - 8.95 | - 8.93 | -18.64 | -16.38 | -15.64 | -10.96 |
| 1.00 | - 5.78 | - 8.95 | - 8.93 | -16.64 | -14.38 | -13.64 | - 9.96 |
| 2.00 | - 5.47 | - 8.95 | - 8.93 | -14.64 | -12.38 | -11.64 | - 8.96 |
| 3.00 | - 5.42 | - 8.95 | - 8.93 | -12.64 | -10.38 | - 9.64 | - 7.96 |
| 4.00 | - 5.42 | - 8.95 | - 8.87 | -10.64 | - 8.38 | - 7.64 | - 6.96 |
| 5.00 | - 5.42 | - 8.95 | - 8.51 | - 8.64 | - 6.38 | - 5.64 | - 5.96 |
| 6.00 | - 5.42 | - 8.95 | - 7.69 | - 6.64 | - 4.38 | - 3.64 | - 4.96 |
| 7.00 | - 5.42 | - 8.95 | - 6.71 | - 4.64 | - 2.38 | - 1.64 | - 3.96 |

| pH | Soot | HCHO | $HO_2$ |
|---|---|---|---|
| 0.00 | -18.02 | -13.58 | -14.98 |
| 1.00 | -17.92 | -12.57 | -14.80 |
| 2.00 | -17.31 | -11.51 | -14.19 |
| 3.00 | -15.78 | -10.12 | -12.55 |
| 4.00 | -14.89 | - 8.28 | -10.20 |
| 5.00 | -12.84 | - 6.30 | - 7.64 |
| 6.00 | -11.95 | - 4.30 | - 5.44 |
| 7.00 | -11.55 | - 2.30 | - 3.42 |

Log Rate (%/hr)

| pH | $H_2O_2$ | $CH_3OOH$ | $CH_3CO_3H$ | PAN | HONO | Fe(III) | Mn(II) |
|---|---|---|---|---|---|---|---|
| 0.00 | 1.38 | - 1.01 | - 0.99 | -10.70 | - 8.43 | - 7.69 | - 3.02 |
| 1.00 | 2.17 | - 1.01 | - 0.99 | - 8.70 | - 6.43 | - 5.69 | - 2.02 |
| 2.00 | 2.47 | - 1.01 | - 0.99 | - 6.70 | - 4.43 | - 3.69 | - 1.02 |
| 3.00 | 2.52 | - 1.01 | - 0.98 | - 4.70 | - 2.43 | - 1.69 | - 0.02 |
| 4.00 | 2.53 | - 1.01 | - 0.92 | - 2.70 | - 0.43 | 0.31 | 0.98 |
| 5.00 | 2.52 | - 1.01 | - 0.57 | - 0.70 | 1.56 | 2.30 | 1.98 |
| 6.00 | 2.49 | - 1.04 | 0.22 | 1.27 | 3.53 | 4.27 | 2.95 |
| 7.00 | 2.18 | - 1.36 | 0.88 | 2.95 | 5.22 | 5.96 | 3.63 |

| pH | Soot | HCHO | $HO_2$ |
|---|---|---|---|
| 0.00 | -10.07 | - 5.64 | - 6.96 |
| 1.00 | - 9.98 | - 4.63 | - 6.86 |
| 2.00 | - 9.37 | - 3.56 | - 6.24 |
| 3.00 | - 7.84 | - 2.18 | - 4.60 |
| 4.00 | - 6.15 | - 0.34 | - 2.26 |
| 5.00 | - 4.90 | 1.64 | 8.38 |
| 6.00 | - 4.04 | 3.60 | 2.46 |
| 7.00 | - 3.96 | 5.29 | 4.17 |

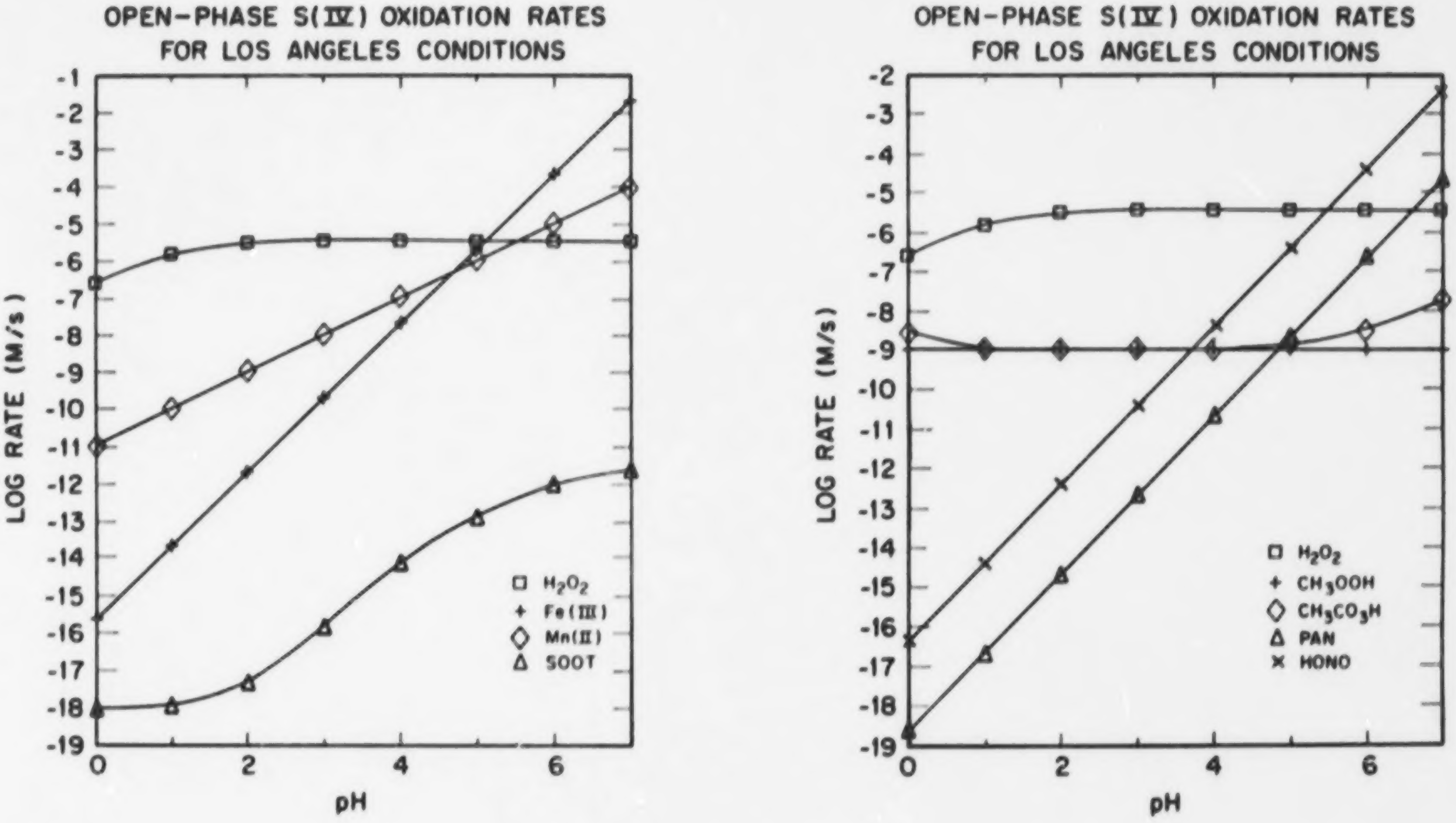
## GAS-PHASE REACTIONS, RATE CONSTANTS AND RATES

| Reaction | k(1/Ms) | Rate(M/s) | LogR-%/h | ppb $SO_2$ | atm $SO_2$ |
|---|---|---|---|---|---|
| $O_3 + SO_2 \longrightarrow O_2 + SO_3$ | 4.80E-03 | 8.03E-21 | -5.45 | 2.00E+01 | 2.00E-08 |
| $HO_2 + SO_2 \longrightarrow HO + SO_3$ | 6.00E+02 | 8.03E-19 | -3.45 | 2.00E+01 | 2.00E-08 |
| $OH + SO_2 + M \longrightarrow HOSO_2$ | 6.60E+07 | 2.21E-16 | -1.01 | 2.00E+01 | 2.00E-08 |
| $N_2O_5 + SO_2 \longrightarrow N_2O_4 + SO_3$ | 2.40E-02 | 3.21E-22 | -6.85 | 2.00E+01 | 2.00E-08 |

## PERCENTAGE CONTRIBUTION TO TOTAL RATE

| vT(pH5-7) | % $O_3$ | % $H_2O_2$ | % OH | % HONO | % Fe(III) | % HCHO | % $HO_2$ | % Mn(II) |
|---|---|---|---|---|---|---|---|---|
| 4.02E+02 | 0.04 | 83.61 | 13.26 | 0.09 | 0.50 | 0.11 | .00 | 2.37 |
| 1.25E+03 | 1.04 | 26.64 | 42.33 | 2.93 | 16.05 | 3.46 | 0.16 | 7.55 |
| 3.37E+04 | 3.50 | 0.92 | 15.15 | 10.15 | 55.70 | 11.97 | 0.87 | 2.62 |
| 1.35E+06 | 4.17 | 0.01 | 2.36 | 12.15 | 66.67 | 14.32 | 1.10 | 0.31 |

In order to understand the potential importance of each reaction over a broad range of pH, a comparison was made of calculated reaction rates for an idealized cloud with a liquid water content (LWC) of 0.2 g/m$^3$ at 25$^0$C and gas-phase concentrations of reactive components typical of the Los Angeles atmosphere. A summary of these calculations is provided in Table 1 for reaction rates in terms of moles/liter-sec on the water side alone and in terms of %/hr with respect to the total volumetric concentration of $SO_2$ (moles/m$^3$). As in the case for many systems of importance in aquatic chemistry, pH is again the master variable for this comparative system of reactions. Figure 1 presents S(IV) oxidation rates for a number of species as a function of pH. As shown in the figure, $H_2O_2$ is clearly the most effective oxidant of S(IV) in an open-phase system over the entire pH range. Below pH 4.0, hydrogen peroxide (see Table K27) appears to be the sole reactant capable of producing environmentally significant S(IV) oxidation rates. Of special interest in Figure 1 is the very low apparent S(IV) oxidation rate shown for the soot-catalyzed reaction given the empirical rate law (see Table K30) reported by Brodzinsky et al. (1980). The maximum rate shown for this reaction at pH 7 is 0.0001 %/hr. It is clearly an inconsequential reaction in terms of aqueous-phase S(IV) oxidation. However, in spite of this fact, the soot-catalyzed system is the subject of much attention in certain laboratories around the country. This prohibitively slow reaction rate is due once again to a second-order kinetic dependence, this time on [S(IV)] in the aqueous phase. In an open-phase system with a gas-phase $SO_2$ concentration of 20 ppb, this squared S(IV) dependence immediately produces a factor of $10^{-15}$ that must be overcome. Even though the reaction appears to be fast under



OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS

OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS

Figure 1

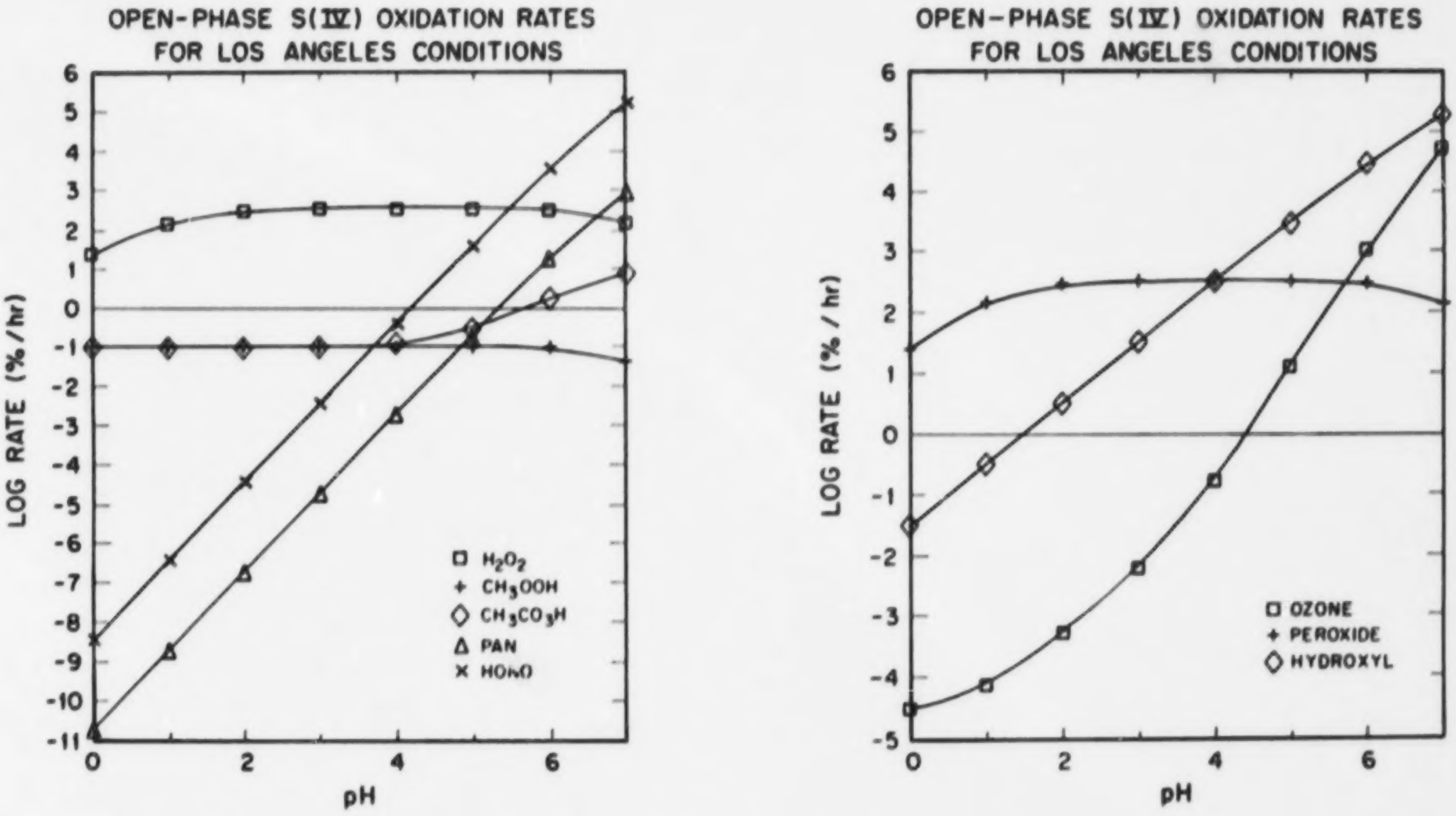
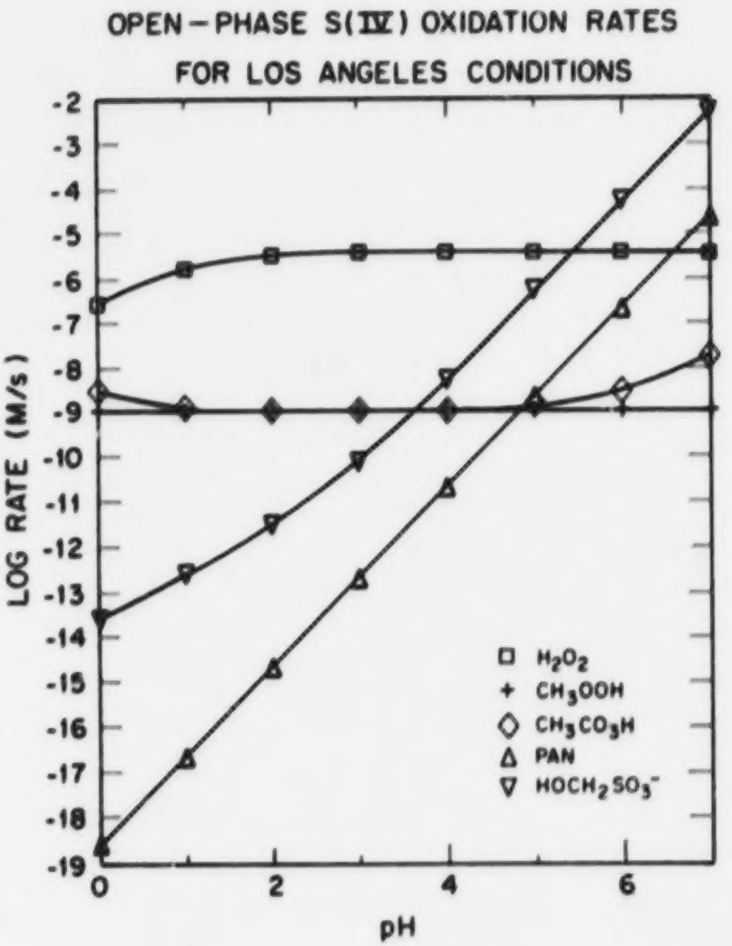
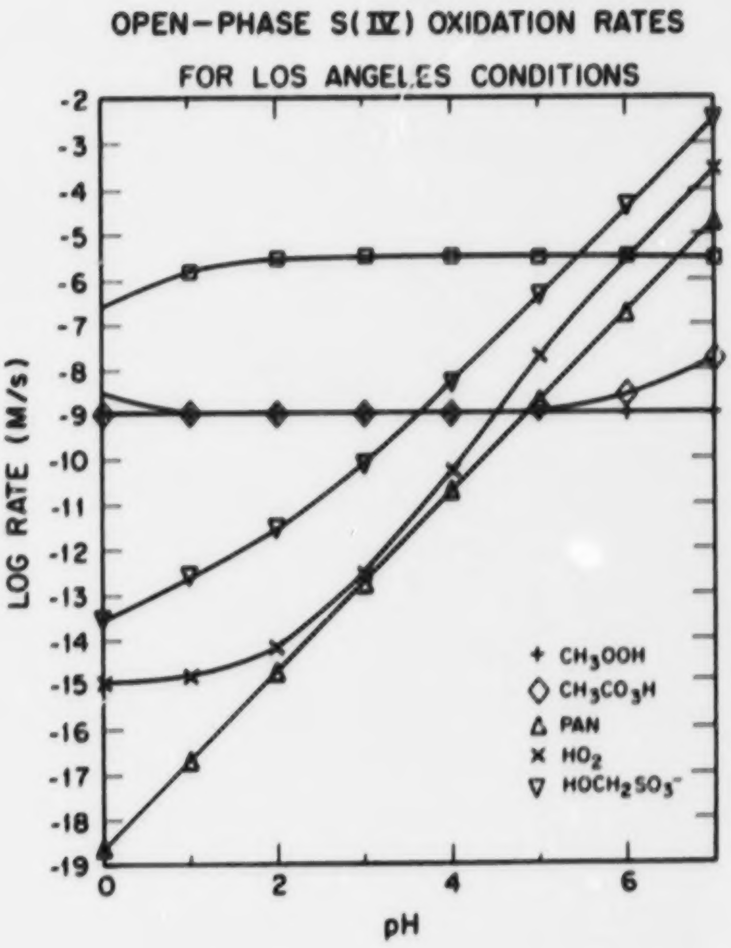
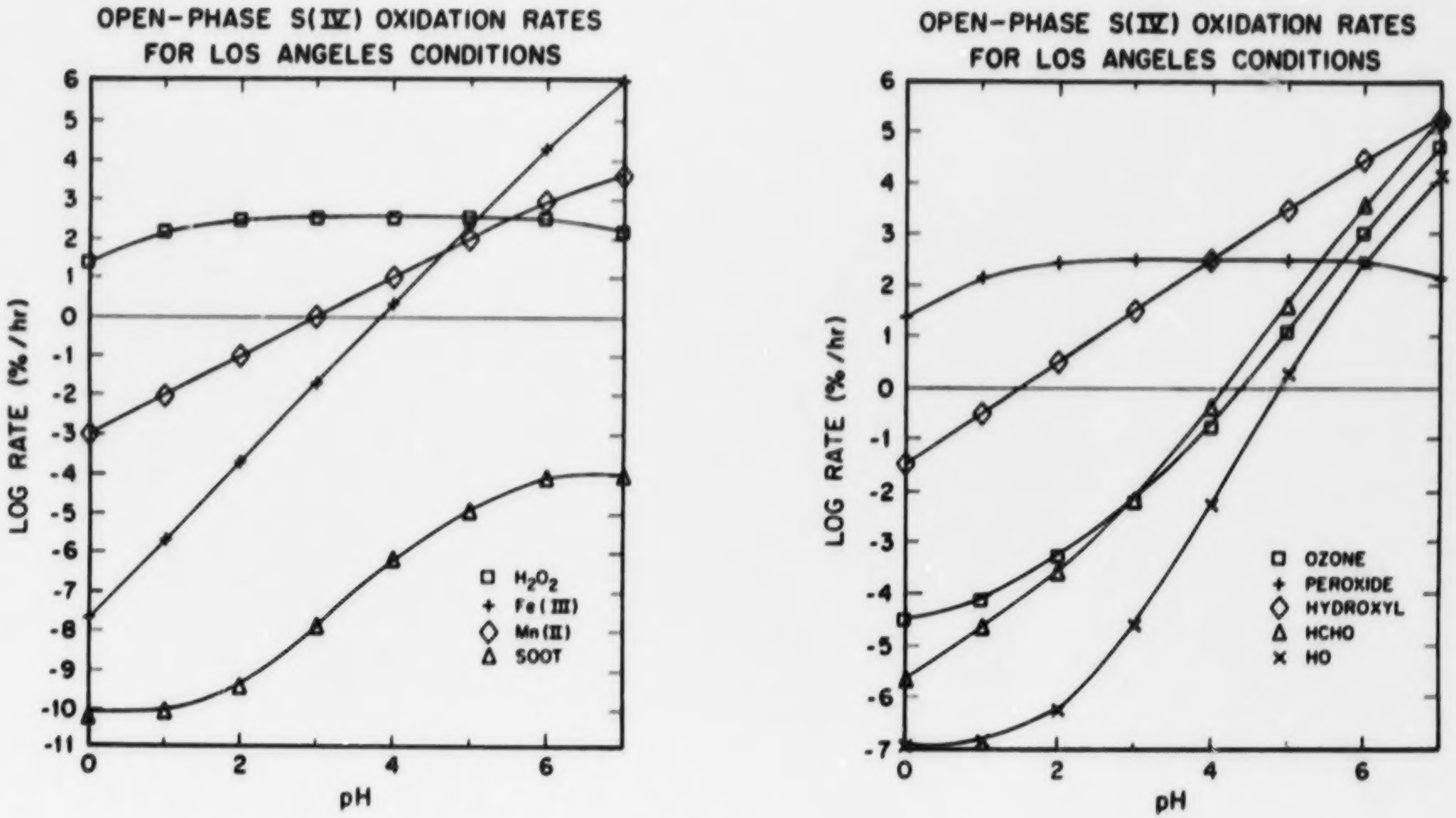


Figure 1 (cont.)


OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS


OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS


OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS

OPEN-PHASE S(IV) OXIDATION RATES FOR LOS ANGELES CONDITIONS

Figure 1 (cont.)

laboratory conditions in a closed-system batch reactor, it is of no consequence in the atmosphere because of the highly unfavorable kinetic dependence on [S(IV)]. The case for soot reactions should be set to rest at this time.

Above pH 4, a number of kinetic pathways in addition to the S(IV)-$H_2O_2$ reaction become viable potential contributors to net S(IV) oxidation. For example, in Figure 1 it is clearly seen that ozone, OH, $HO_2$, HONO and Fe(III)- and Mn(II)-catalyzed autoxidation are major contributors to S(IV) oxidation above pH 4. With an idealized "sticking coefficient" of 1.0 for OH, the OH pathway may proceed as rapidly as 500 %/hr at pH 5.0. Likewise, the predicted conversion rate for the above reactants at pH 5.0 are as follows: $H_2O_2$ (331 %/hr), $O_3$ (131 %/hr), $HO_2$ (2.0 %/hr), HONO (36.3 %/hr), Fe(III)/$O_2$ (200.0 %/hr), and Mn(II)/$O_2$ (95.5 %/hr). At slightly higher pH, PAN and peroxyacetic acid will contribute somewhat to the net S(VI) production rate.

In addition to the oxidation pathways for S(IV) mentioned above, one additional pathway for transformation was considered in this inter-comparison. That pathway is the reversible formation of hydroxymethanesulfonate from the in situ reaction between HCHO and S(IV). The details of the thermodynamics of this system is presented in Tables T13-T16 of Appendix B. Evidence for the existence of bisulfite-aldehyde addition complexes in clouds and fogs has been presented by Munger et al. (1983; 1984) and Richards et al. (1983). In our laboratory, we have actually isolated and quantified these complexes from cloud and fog samples taken in the Los Angeles basin and the San Joaquin Valley of California using ion-pairing ion chromatography. We have definitive evidence for the frequent occurrence of hydroxymethane sulfonate and a-hydroxymethanesulfonate. Concentrations as high as 1.0 mM have been observed. Given the kinetic data and rate law of Boyce and Hoffmann (1984) as shown in Table 1, the calculated formation rate of $HOCH_2SO_3^-$ at pH 5.0 is 43.6 %/hr and at pH 7.0 it is $1.95 \times 10^5$ %/hr. These results suggest that RCHO/S(IV) adducts form preferentially near sources of $SO_2$ and RCHO in near neutral aquated haze aerosol. Because of the extremely slow dissociation kinetics for these adducts, the sulfonate complexes are metastable in more acidic environments with lower $P_{SO2}$ and $P_{RCHO}$. Unfavorable reaction kinetics at pH 3 does not necessarily mean that these adducts should not be found. It does indicate that proximity to sources and transport considerations are very important. The formation constants for a wide variety of these adducts are quite large (i.e., $> 10^4\ M^{-1}$) as shown in Tables T13 and T14.

From the figures it is abundantly clear that the principal oxidant of S(IV) in most cloud systems will be hydrogen peroxide. However, for those clouds in the pH domain of 4 to 7, the other oxidants may play an important role. To indicate this critical transition more concisely, the kinetic results tabulated in Table 1 have been plotted in terms of the percentage contribution to total transformation rate as a function of pH clustered with respect to the most important reactants (see Figure 3). From this figure the relative importance of $H_2O_2$, OH and Fe(III)/$O_2$ can be seen. At pH 4, peroxide is clearly dominant, while at pH 7, Fe(III)/oxygen dominates. Even though the OH reaction rate is significantly high at pH 7, the iron catalyzed rate is clearly overwhelming. Ozone, HCHO, and HONO contribute less substantially to transformation than the above oxidants. In Figure 4 the rate of production of S(VI) at pH 5 is compared to the respective gas-phase

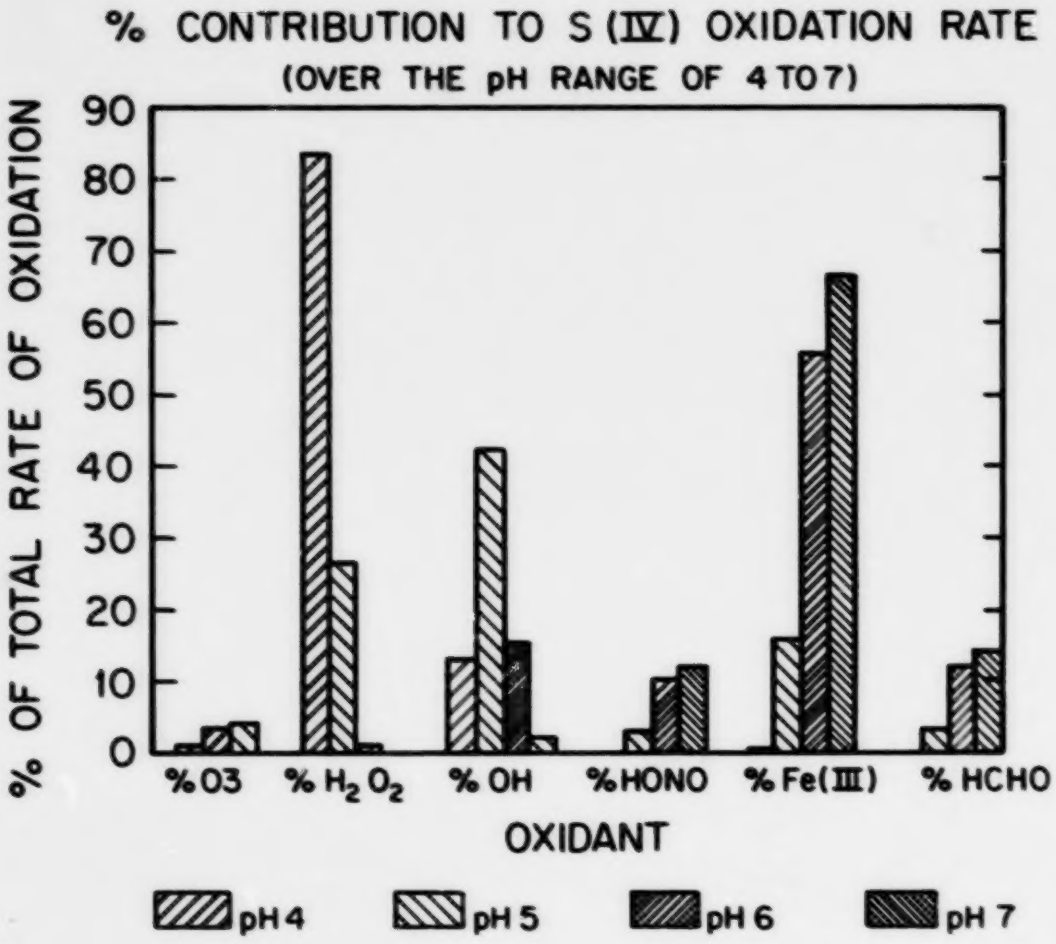

% CONTRIBUTION TO S(IV) OXIDATION RATE
(OVER THE pH RANGE OF 4 TO 7)
% OF TOTAL RATE OF OXIDATION
0
10
20
30
40
50
60
70
80
90
% O3
% $H_2O_2$
% OH
% HONO
% Fe(III)
% HCHO
OXIDANT
pH 4
pH 5
pH 6
pH 7

Figure 2

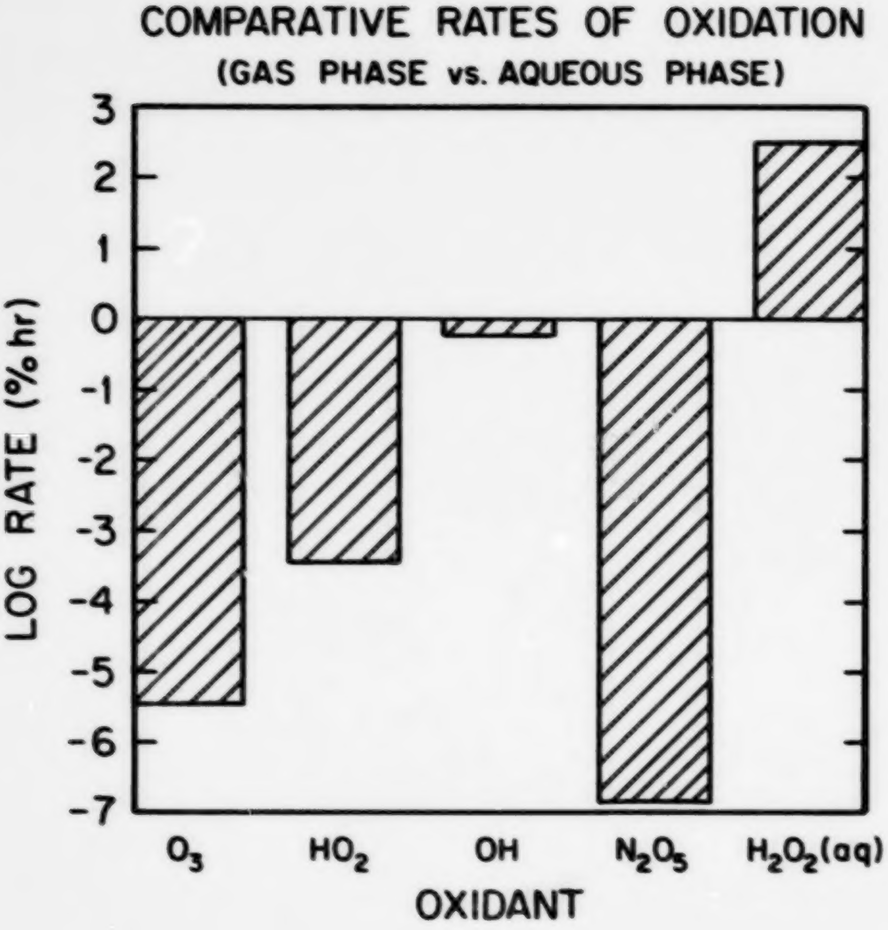

COMPARATIVE RATES OF OXIDATION
(GAS PHASE vs. AQUEOUS PHASE)
LOG RATE (%/hr)
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
$O_3$
$HO_2$
OH
$N_2O_5$
$H_2O_2$(aq)
OXIDANT

Figure 3

conversion rates, which were calculated from kinetic data given by Calvert and Stockwell (1984). The concentrations for the gas-phase oxidants were taken as their respective, optimal daily steady-state values. As shown in Figure 3, the gas-phase pathways are not competitive with the aqueous-phase pathways considered above. Of course, many other investigators have pointed out this conclusion before.

## B. CRITICAL EVALUATION OF KINETIC DATA

All of the available kinetic data for the above S(IV)/oxidant systems has been compiled and critically evaluated. Chapter III is devoted to the critical evaluation of the ozone/S(IV) system (Table K26). A detailed treatment of the S(IV)/HCHO system is given in Boyce and Hoffmann (1983). Details of reaction mechanisms for other systems are discussed in Hoffmann and Jacob (1984).

In the case of hydrogen peroxide, all the pertinent kinetic data is summarized in Table K27. The reaction is now well-understood (McArdle and Hoffmann, 1983) to proceed via a nucleophilic displacement by hydrogen peroxide on bisulfite as the principal reactive S(IV) species. The reaction is unique with respect to the other systems in that it is acid catalyzed. This means that in an open-system the net effect of a lowering of pH will be nill in that the increase in reaction rate due to a drop in pH will be offset by the decrease in [S(IV)] which is dependent on the term $([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})/[H^+]^2$. Below pH 1.0 the reaction rate begins to decrease with a further decrease in pH due to the effects of the above term and due to the decrease in $[HSO_3^-]$. Given in Table K27 is the recommended rate expression that should be used in all further modeling efforts. Along with this rate expression are critically-evaluated rate constants and activation parameters. These constants have been obtained by consideration of all available kinetic data treated using the recommended rate expression. Therefore, the results on the third page of Table K27 represent a self-consistent rate law and kinetic constants to be used with this rate law. This and other self-consistent rate laws given in Tables K26 and K29 are fundamental kinetic expressions that are derived from step-wise reaction mechanisms. As such these self-consistent rate expressions should be used preferentially over the empirical rate laws of a single investigation. Table K26 gives the same analysis for ozone/S(IV); Table K28 gives the unified treatment for Fe(III)-$O_2$/S(IV); and Table K29 gives an identical treatment for the Mn(II)/$O_2$ reaction system. For other reaction systems under consideration in Tables K1 through K31, only one or two kinetic studies are available and as a consequence no attempt has been made to unify the results.

# CHAPTER III

# KINETICS OF THE S(IV)-$O_3$ REACTION

## A. OVERVIEW

Kinetic data obtained by a number of different investigators on the reaction of S(IV) with ozone in aqueous solution has been analyzed in terms of a single self-consistent rate expression. The rate expression that most appropriately fits all kinetic observations treated in this study is:

$$-d[S(IV)]/dt = (k_0a_0 + k_1a_1 + k_2a_2)[S(IV)][O_3]$$

where

$$a_0 = [H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

$$a_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

$$a_2 = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

This kinetic expression is similar in form to the empirical rate laws reported by Erickson et al. (1977) and Hoigne et al. (1984). The recommended values for $k_0$, $k_1$, and $k_2$ are $(2.4 \pm 1.1) \times 10^4$ $M^{-1}s^{-1}$, $(3.7 \pm 0.7) \times 10^5$ $M^{-1}s^{-1}$, and $(1.5 \pm 0.6) \times 10^9$ $M^{-1}s^{-1}$, respectively. The activation energies that are recommended for $k_1$ and $k_2$ are taken from Erickson et al. (1977) as 46.0 kJ/mol and 43.9 kJ/mol, respectively. The reaction proceeds via three independent pathways that involve an

nucleophilic attack on ozone by $SO_3^=$, $HO\text{-}SO_2^-$, and $SO_2 \cdot H_2O$. Arguments for the existence of $HO\text{-}SO_2^-$ as the predominant form of bisulfite in aqueous solution are presented. Rate laws and kinetic data of five investigators are compared for an open cloud water system with a liquid water content of 0.2 $g/m^3$.

## B. INTRODUCTION

Oxidation of sulfur dioxide by oxygen, ozone, nitrogen dioxide, or hydrogen peroxide in aqueous microdroplets or hydrometeors has been acknowledged as a viable non-photolytic pathway for the production of sulfuric acid in fogs, clouds and humid atmospheres (Hoffmann and Boyce, 1983; Hoffmann and Jacob, 1984; Jacob and Hoffmann, 1983). Oxidation by either ozone, hydrogen peroxide, or the combination of the two has been shown to be a particularly important S(IV)-conversion pathway in clouds and fogs (Jacob and Hoffmann, 1983; Martin, 1983; Martin, 1984; Hegg and Hobbs, 1982). Martin (1983) has recently analyzed data obtained by Hegg and Hobbs (1982) for the production of sulfate in wave clouds in terms of the known kinetics of ozone oxidation of sulfur(IV) (i.e., total aquated sulfur dioxide). He has shown that the observed transformation rates of Hegg and Hobbs can be interpreted quantitatively in terms of the kinetic data of Maahs (1983a,b). The correlation between predicted and observed sulfate production rates as a function of pH is reasonably high.

Ozone can be classified as a "fast oxidant" of sulfur dioxide in the pH range $\geq$ 4 along with hydrogen peroxide and nitrous acid (Martin, 1984). However, the above oxidants are substantially less abundant than oxygen, which is a competitive oxidant in aqueous solution (Hoffmann and

Boyce, 1983; Hoffmann and Jacob, 1984; Boyce et al., 1983). In spite of their lower gas-phase concentrations, hydrogen peroxide and ozone have significantly higher Henry's Law Constants (Jacob and Hoffmann, 1983) than oxygen. This feature combined with their unusual reactivity make them highly competent oxidants both thermodynamically and kinetically.

The kinetics of the reaction (eqn. 3.1) of sulfur(IV) and ozone has been studied by a number of investigators.

$$HSO_3^- + O_3 \longrightarrow H^+ + SO_4^= + O_2 \qquad (3.1)$$

Penkett (1972), Penkett et al. (1979), Erickson et al. (1977), Larson et al. (1978), Harrison et al. (1982), Maahs (1983a,b), Hoigne et al. (1984), and Martin (1984) have studied the kinetics of this reaction over a broad pH range of -0.3 to 7.0. A summary of empirical rate laws and observed rate constants reported by these investigators is presented in Table 2. There appears to be reasonable agreement among the investigators in principle for the rate of the reaction over a limited pH range as determined by the cluster of observed rate constants in the range of $10^4$ to $10^5$ $M^{-1}s^{-1}$. However, there appears to be less agreement with respect to the overall kinetic order; in particular there is some disagreement as to the exact reaction order with respect to $[H^+]$. The work of Erickson et al., Maahs, and Hoigne et al. indicates that the overall rate of reaction is described by a multi-term rate law. Erickson et al. and Hoigne et al. have used basically the same three-term rate law to describe the kinetics over the pH range of -0.3 to 7.0. They have found that all three of the major S(IV) species, $H_2O{\cdot}SO_2$, $HSO_3^-$, and $SO_3^=$ react with ozone via separate kinetic pathways

TABLE 2. EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) BY OZONE

| Rate ($v = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $v = k_1[HSO_3^-][O_3] + k_2[SO_3^{2-}][O_3]$ | $k_1 = 3.1 \times 10^5 M^{-1} s^{-1}$<br>$E_{a,1} = 46$ kJ mol$^{-1}$<br>$k_2 = 2.2 \times 10^9 M^{-1} s^{-1}$<br>$E_{a,2} = 43.9$ kJ mol$^{-1}$ | pH 0-4<br>T = 25°C | Erickson et al. (1977) |
| $v = (k_o[H_2O \cdot SO_2] + k_1[HSO_3^-] + k_2 [SO_3^{2-}])[O_3]$ | $k_o = (2 \pm 2) \times 10^4 M^{-1} s^{-1}$<br>$k_1 = (3.2 \pm 0.2) \times 10^5 M^{-1} s^{-1}$<br>$k_2 = (1.0 \pm 0.2) \times 10^9 M^{-1} s^{-1}$ | pH 1-6<br>T = 22°C | Hoigne et al. (1984) |
| $v = (k_1 + k_2 [H^+]^{-1})[S(IV)][O_3]$ | $k_1 = 4.39 \times 10^{11} e^{-4131/T} (\pm 3 \times 10^4) M^{-1} s^{-1}$<br>$k_2 = 2.56 \times 10^3 e^{-966/T} (\pm 15)\ s^{-1}$<br>$\log k = \log k_o + (\sqrt{\mu}/(1 + \sqrt{\mu})) - 0.3\mu$ | pH 3-6.2<br>T = 10-25°C<br>$\mu$ = 0.001-0.4M | Maahs (1983)<br>(1983) |

TABLE 2 (continued)

| Rate ($v = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $v = k\,[O_3][S(IV)][H^+]^{-0.5}$ | $k = 1.9 \times 10^4 M^{-0.5} s^{-1}$ | pH 0-3<br>T = 25°C | Martin (1984) |
| $v = k\,[O_3][HSO_3^-][H^+]^{-0.5}$ | $k = (1.45 \pm 0.7) \times 10^4 M^{-0.5} s^{-1}$ | pH 1-5<br>T = 25°C | Penkett et al. (1979) |
| $v = kP_{O_3}H_{O_3}[HSO_3^-][H^+]^{-0.1}$ | $k = 4.4 \times 10^4 M^{-0.9} s^{-1}$ | pH 4-7<br>T = 25°C | Larson et al. (1978) |
| $v = k[Fe^{3+}][S(IV)][O_3][H^+]^n$ | $k_{obs} = 6.8 \times 10^5 M^{-1} min^{-1} ppm^{-1}$ | pH 4-6<br>T = 22°C<br>$[Fe^{3+}] \geq 10\mu M$ | Harrison et al. (1982) |

to give S(VI) and oxygen. These investigators have reported individual second-order rate constants for each pathway. The work of Maahs is in general agreement with the results of Erickson et al. and Hoigne et al. He has interpreted his results primarily in terms of a single reactive S(IV) species, $HSO_3^-$, which then reacts with ozone via two separate pathways one of which is based-catalyzed. As will be shown in subsequent paragraphs the empirical rate law of Maahs' is virtually identical to those of Erickson et al. and Hoigne et al. when algebraically rearranged. The work of Penkett et al. and Martin clusters into another identifiable group in terms of the form of the empirical rate law and the magnitude of the observed rate constant. Reasons for this somewhat fortuitous agreement over a wide range of pH will be discussed in later portions of this chapter. The work of Larson et al. and Harrison et al. shows less general agreement with the other investigators. Possible reasons for this disagreement have already been discussed by Maahs (1983b). There is clearly less agreement among the various investigators as to the mechanism(s) of the reaction. Penkett et al. favor a free radical mechanism that involves OH, $HSO_3$, and $HSO_5$ as primary radicals; whereas Maahs (1983b) favors a polar pathway that proceeds via an electrophilic attack of $O_3$ on the sulfur atom of $HOSO_2^-$, $HSO_3^-$, or perhaps $SO_3^=$. It should be pointed out that Maahs' proposed mechanism fails to account for the isotopic labelling experiments of Espenson and Taube (1965) that showed the incorporation of two labelled oxygen atoms into the product sulfate even though the stoichiometry (eqn. 1) requires the addition of only one oxygen atom to the reactant.

Future efforts in development of comprehensive atmospheric chemistry models, that incorporate aqueous-phase reactions, will require a self-consistent set of rate expressions, rate constants, and activation parameters applicable over a broad range of conditions (i.e., pH, concentration, and temperature). The goals of this chapter are to analyze the composite set of data and observations reported by the above investigators in terms of a self-consistent rate expression, and to propose a mechanism(s) that is consistent with the generalized rate expression and with the ancillary mechanistic information such as the reported isotopic results and ionic strength dependence.

## C. RESULTS AND DISCUSSION

The raw kinetic data of Erickson et al. (1977), Hoigne et al. (1984), Maahs (1983b), Martin (1984), and Penkett et al. (1979) were analyzed in terms of the three-term rate law favored by Erickson et al. and Hoigne et al. Results of that analysis are presented in Table 3.2. The observed kinetic data of Maahs, Penkett et al., and Martin can be reinterpreted in terms of a multi-term rate law of the following form:

$$-d[S(IV)]/dt = (k_0a_0 + k_1a_1 + k_2a_2)[S(IV)][O_3] \qquad (3.2)$$

## TABLE 3. INTRINSIC RATE LAW FOR THE OXIDATION OF S(IV) BY OZONE

Based on data from Erickson et al. (1977), Hoigne et al. (1984),
Maahs (1983), Martin (1984), and Penkett et al. (1979).

$\nu = -d[S(IV)]/dt = (k_o\alpha_o + k_1\alpha_1 + k_2\alpha_2)\,[S(IV)][O_3]$

$\alpha_o = [H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ $\qquad [SO_2 \cdot H_2O] = \alpha_o[S(IV)]$

$\alpha_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ $\qquad [HSO_3^-] = \alpha_1[S(IV)]$

$\alpha_2 = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ $\qquad [SO_3^{2-}] = \alpha_2[S(IV)]$

$\alpha_o + \alpha_1 + \alpha_2 = 1$ $\qquad [S(IV)] = [H_2O \cdot SO_2] + [HSO_3^-] + [SO_2^{2-}]$

| | **Erickson** | **Hoigne** | **Maahs** | **Penkett** | **Martin** |
|---|---|---|---|---|---|
| $k_o(M^{-1}s^{-1})$ | ~ 5.9 X $10^2$ | (2.0 ± 2.0) X $10^4$ | — | 1.6 X $10^4$ | 3.7 X $10^4$ |
| $k_1(M^{-1}s^{-1})$ | 3.1 X $10^5$ | (3.2 ± 0.2) X $10^5$ | 3.9 X $10^5$ | 4.5 X $10^5$ | 1.2 X $10^6$ |
| $k_2(M^{-1}s^{-1})$ | 2.2 X $10^9$ | (1.0 ± 0.2) X $10^9$ | 1.2 X $10^9$ | — | — |
| $E_{a,1}$(kJ mol$^{-1}$) | 46.0 | — | 33.9 | 30.0 | — |
| $E_{a,2}$(kJ mol$^{-1}$) | 43.9 | — | 30.7 | — | — |

where

$$a_0 = [H^+]^2/([H^+]_2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad (3.3)$$

$$a_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad (3.4)$$

$$a_2 = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad (3.5)$$

$$a_0 + a_1 + a_2 = 1 \qquad (3.6)$$

$$[S(IV)] = [H_2O\cdot SO_2] + [HSO_3^-] + [SO_3^=] \qquad (3.7)$$

$$[H_2O\cdot SO_2] = a_0[S(IV)] \qquad (3.8)$$

$$[HSO_3^-] = a_1[S(IV)] \qquad (3.9)$$

$$[SO_3^=] = a_2[S(IV)] \qquad (3.10)$$

The above rate law is algebraically equivalent in form to those used by Erickson et al. and Hoigne et al. with a few notational differences. The constants, $k_0$, $k_1$, and $k_2$ show reasonable agreement for all five groups. The constants of Erickson et al., Hoigne et al., and Maahs show the closest agreement which appears to reflect carefully controlled experiments. The range (pH 0-3) of experimental conditions used by Martin (1984) precluded the determination of $k_2$ from his data; while the experimental conditions used by Penkett et al. (1979) (i.e., no pH control during a kinetic run) limited his data to the values of $k_0$ and

$k_1$. In the experiments of Penkett et al. at higher pH, the pH was not held constant during the course of a stopped-flow kinetic run. Given the magnitude of $k_2$ the third term of the rate law can be shown to dominate the overall observed rate between pH 4 and 5. With the extremely rapid production of $H^+$ in this pH domain, the pH of the reacting solution dropped to below pH 4. In this pH range, Penkett et al.'s observed kinetic results reflected primarily the $k_1$ term. Therefore when they assumed that they were following the reaction at pH 5 they were in fact observing changes at much lower pH. The data generated by Maahs (1983b) at higher pH is reliable because he employed buffers to maintain pH constant. The data of Erickson et al. were obtained in a pH domain in which the in situ production of acidity had a negligible impact on the pH of the reacting solution. Martin's data were collected over a similar pH range although his data yield an intrinsic value of $k_1$ which is approximately a factor of three higher than the other four research groups. There is no obvious explanation for this discrepancy.

In general the kinetic data of Erickson et al., Maahs, and Hoigne appears to be the most self-consistent and reliable for application over a broad range of pH. A detailed analysis of the generalized rate law of eqn. 2 for all of the above investigators is presented in Table 4. Both open-phase (i.e., gas transfer is allowed to take place across a gas-water interface) and closed-phase (i.e., homogeneous aqueous phase reactions only) systems involving S(IV), $O_3$, and $H^+$ are considered. Values for $K_{a1}$, $K_{a2}$, $H_{SO2}$, and $H_{O3}$ have been taken from Jacob and Hoffmann (1983); the liquid water content (LWC) of the cloud water

## Table 4. Kinetic Data Analysis for the S(IV)-Ozone Reaction

**Input Data: Equilibrium Constants, pH, Partial Pressures, Temperature**

| | | | |
|---|---|---|---|
| $H(SO_2)$ | 1.24 (M/atm) | $pK_1$ | 1.89 |
| $H(O_3)$ | 0.01 (M/atm) | $pK_2$ | 7.22 |
| $P(SO_2)$ | 2.00E-08 (atm) | T(oC) | 25.00 |
| $P(O_3)$ | 5.00E-08 (atm) | pH | 5.00 |

**Rate Law, Concentrations, Constants, and Ionization Fractions**

| | | | |
|---|---|---|---|
| $-\log [H^+]$ | 1.00E-05 | $R = (k_0a_0+k_1a_1+k_2a_2)[S(IV)][O_3]$ | |
| $-\log K_1$ | 1.29E-02 | $[S(IV)] = H(SO_2)P(SO_2)/a_0$ | |
| $-\log K_2$ | 6.03E-08 | $[O_3] = H(O_3)P(O_3)$ | |
| $a_0$ | 7.71E-04 | DEN | 1.30E-07 |
| $a_1$ | 9.93E-01 | [S(IV)] | 3.22E-05 |
| $a_2$ | 5.98E-03 | $[O_3]$ | 4.67E-10 |

**Rate Constants, Activation Energies, Reaction Rates per Investigator**

| | Erickson | Maahs | Hoigne | Penkett | Martin |
|---|---|---|---|---|---|
| $k_0$ (1/Ms) | ******** | ******** | 2.00E+04 | 1.60E+04 | 3.70E+04 |
| $k_1$ (1/Ms) | 3.10E+05 | 3.90E+05 | 3.20E+05 | 4.50E+05 | 1.20E+06 |
| $k_2$ (1/Ms) | 2.20E+09 | 1.20E+09 | 1.00E+09 | ******** | ******** |
| Temp (°C) | 25.00 | 25.00 | 22.00 | 25.00 | 25.00 |
| $Ea,k_1$ (kJ/mol) | 46.00 | 33.90 | ***** | ***** | ***** |
| $Ea,k_2$ (kJ/mol) | 43.90 | 30.70 | ***** | ***** | ***** |
| Rate (M/s) | 2.02E-07 | 1.14E-07 | 9.46E-08 | 6.71E-09 | 1.79E-08 |
| Rate (M/hr) | 7.28E-04 | 4.09E-04 | 3.40E-04 | 2.41E-05 | 6.44E-05 |
| LWC ($g/m^3$) | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Rate ($mol/m^3hr$) | 1.46E-07 | 8.18E-08 | 6.81E-08 | 4.83E-09 | 1.29E-08 |
| $P(SO_2)/rT$ ($mol/m^3$) | 8.18E-07 | 8.18E-07 | 8.18E-07 | 8.18E-07 | 8.18E-07 |
| Rate (%/hr) | 1.78E+01 | 1.00E+01 | 8.32E+00 | 5.90E-01 | 1.57E+00 |

### log Rate (M/s)

| pH | Erickson | Maahs | Hoigne | Penkett | Martin |
|---|---|---|---|---|---|
| 0.00 | -13.34 | -13.24 | -12.55 | -12.60 | -12.22 |
| 1.00 | -12.33 | -12.23 | -12.15 | -12.07 | -11.65 |
| 2.00 | -11.32 | -11.23 | -11.29 | -11.16 | -10.74 |
| 3.00 | -10.18 | -10.16 | -10.24 | -10.17 | - 9.75 |
| 4.00 | - 8.61 | - 8.78 | - 8.86 | - 9.17 | - 8.75 |
| 5.00 | - 6.69 | - 6.94 | - 7.02 | - 8.17 | - 7.75 |
| 6.00 | - 4.70 | - 4.97 | - 5.04 | - 7.17 | - 6.75 |
| 7.00 | - 2.70 | - 2.97 | - 3.05 | - 6.17 | - 5.75 |

### log Rate (%/hr)

| | | | | | |
|---|---|---|---|---|---|
| 0.00 | - 5.39 | - 5.29 | - 4.61 | - 4.65 | - 4.27 |
| 1.00 | - 4.39 | - 4.29 | - 4.20 | - 4.12 | - 3.71 |
| 2.00 | - 3.37 | - 3.28 | - 3.35 | - 3.22 | - 2.79 |
| 3.00 | - 2.24 | - 2.22 | - 2.30 | - 2.23 | - 1.80 |
| 4.00 | - 0.67 | - 0.84 | - 0.92 | - 1.23 | - 0.80 |
| 5.00 | 1.25 | 1.00 | 0.92 | - 0.23 | 0.20 |
| 6.00 | 3.24 | 2.98 | 2.90 | 0.77 | 1.20 |
| 7.00 | 5.24 | 4.98 | 4.90 | 1.77 | 2.20 |

### Contribution to the Overall Rate of S(IV) Oxidation by Term Using the Data of Hoigne et al. (1984) for an Open System

| pH | $v_0$ | $v_1$ | $v_2$ | $v_T$ | log $v_0$ | log $v_1$ | log $v_2$ | log $v_T$ |
|---|---|---|---|---|---|---|---|---|
| -1.00 | 2.31E-13 | 4.77E-15 | 8.98E-20 | 2.36E-13 | -12.64 | -14.32 | -19.05 | -12.63 |
| 0.00 | 2.31E-13 | 4.77E-14 | 8.98E-18 | 2.79E-13 | -12.64 | -13.32 | -17.05 | -12.55 |
| 1.00 | 2.31E-13 | 4.77E-13 | 8.98E-16 | 7.09E-13 | -12.64 | -12.32 | -15.05 | -12.15 |
| 2.00 | 2.31E-13 | 4.77E-12 | 8.98E-14 | 5.09E-12 | -12.64 | -11.32 | -13.05 | -11.29 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3.00 | 2.31E-13 | 4.77E-11 | 8.98E-12 | 5.69E-11 | -12.64 | -10.32 | -11.05 | -10.24 |
| 4.00 | 2.31E-13 | 4.77E-10 | 8.98E-10 | 1.38E-09 | -12.64 | - 9.32 | - 9.05 | - 8.86 |
| 5.00 | 2.31E-13 | 4.77E-09 | 8.98E-08 | 9.46E-08 | -12.64 | - 8.32 | - 7.05 | - 7.02 |
| 6.00 | 2.31E-13 | 4.77E-08 | 8.98E-06 | 9.03E-06 | -12.64 | - 7.32 | - 5.05 | - 5.04 |
| 7.00 | 2.31E-13 | 4.77E-07 | 8.98E-04 | 8.99E-04 | -12.64 | - 6.32 | - 3.05 | - 3.05 |

Data of Hoigne et al. (1984) for a Closed System with [S(IV)] = 1.00E-05
$[O_3]$ = 1.00E-05

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| -1.00 | 2.00E-06 | 4.12E-08 | 7.75E-13 | 2.04E-06 | - 5.70 | - 7.39 | -12.11 | - 5.69 |
| 0.00 | 1.97E-06 | 4.07E-07 | 7.66E-11 | 2.38E-06 | - 5.70 | - 6.39 | -10.12 | - 5.62 |
| 1.00 | 1.77E-06 | 3.65E-07 | 6.88E-09 | 5.43E-06 | - 5.75 | - 5.44 | - 8.16 | - 5.27 |
| 2.00 | 8.74E-07 | 1.80E-05 | 3.39E-07 | 1.92E-05 | - 6.06 | - 4.74 | - 6.47 | - 4.72 |
| 3.00 | 1.44E-07 | 2.97E-05 | 5.59E-06 | 3.54E-05 | - 6.84 | - 4.53 | - 5.25 | - 4.45 |
| 4.00 | 1.54E-08 | 3.17E-05 | 5.98E-05 | 9.25E-05 | - 7.81 | - 4.50 | - 4.22 | - 4.04 |
| 5.00 | 1.54E-09 | 3.18E-05 | 5.98E-04 | 6.30E-04 | - 8.81 | - 4.50 | - 3.22 | - 3.20 |
| 6.00 | 1.46E-10 | 3.02E-05 | 5.68E-03 | 5.71E-03 | - 9.83 | - 4.52 | - 2.25 | - 2.24 |
| 7.00 | 9.69E-12 | 2.00E-05 | 3.76E-02 | 3.76E-02 | -11.01 | - 4.70 | - 1.42 | - 1.42 |

droplets ($D_p$ = 10 microns) was assumed to be 0.2 $g/m^3$ at 25°C; the overall rate of reaction was assumed to be free of mass transfer limitations, even though this assumption may be somewhat tenuous at higher pH (Martin, 1983). Reaction rates per investigator are given initially for pH 5 and then in subsequent tabulations in Table 4 for the pH ranges of 0 to 7 and -1 to 7. Shown in Figures 4 and 5 are the calculated reaction rates for an open-phase system with gas phase concentrations of $P_{SO2}$ = 20 ppb and $P_{O3}$ = 50 ppb for each investigator using the unified rate law of eqn. 3.2 and the constants given in Tables 3 and 4. Fairly close agreement is shown for all the groups over the pH range 1 to 4. In this pH domain the $k_1$ term is dominant. The slightly higher value for $k_1$ from Martin's data shows up clearly in these comparisons. Over the pH range of 4 to 7 there is much greater discrepancy among the investigators represented in this analysis. This is due to the fact that the $k_2$ term begins to dominate above pH 4. Since $k_2$ values could not be extracted from the Martin and Penkett et al. data sets, they were not factored into the overall rate expression. Erickson et al., Maahs, and Hoigne et al. show overall conversion rates that are a factor of 100 higher than the rates predicted by Martin and Penkett et al. at pH 6. At pH 5 given the above conditions the former groups predict an overall conversion rate with respect to the gas phase $[SO_2]$ of 10 %/hr while the latter groups predict a rate of only 1 %/hr.

The pH dependency of the overall reaction rate can be seen more clearly in Figures 6 and 7 for an open and closed reaction system, respectively. Kinetic constants from the Hoigne et al. data set have been used to construct these plots. The complex pH dependency for the closed-system reaction is shown as Figure 7. Since all of the above

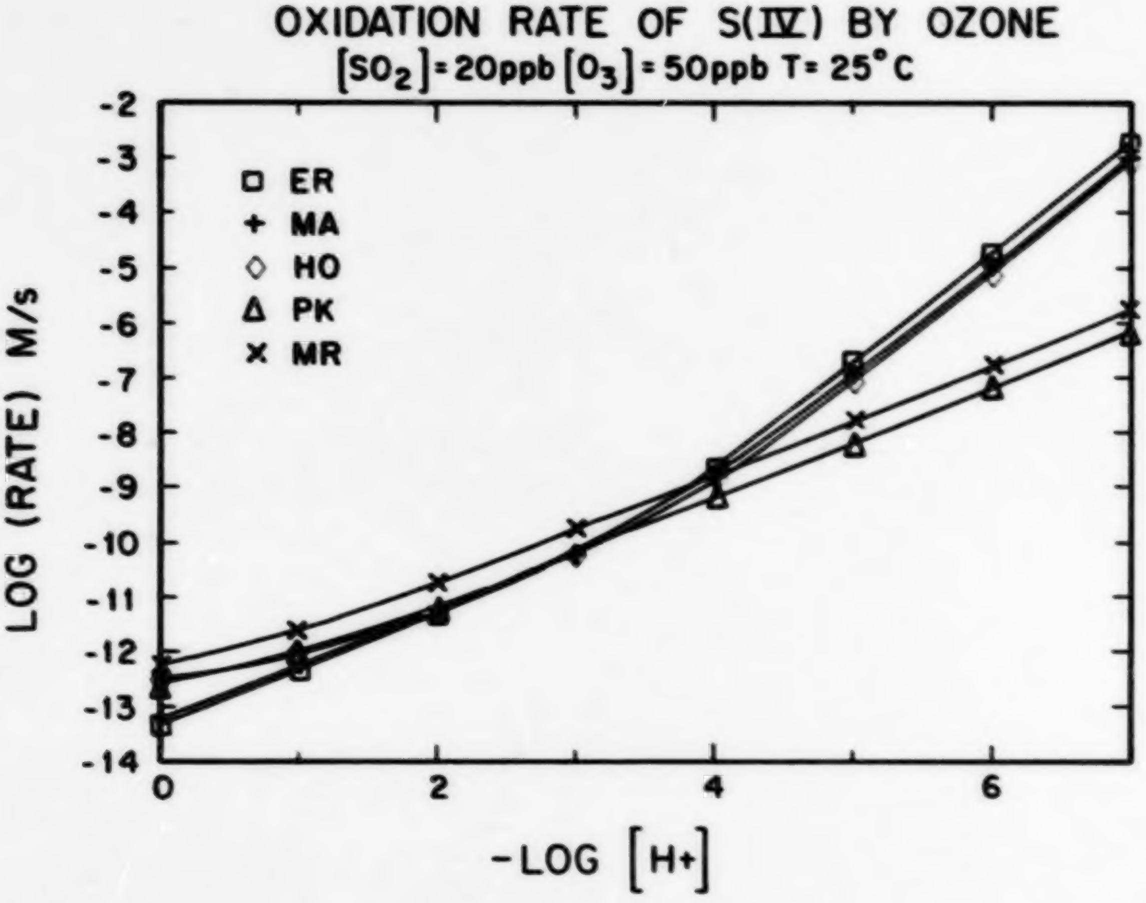


Figure 4. A comparison plot of the rate of S(IV) oxidation by ozone as a function of pH predicted by the empirical rate laws of Table 2 for gas-phase concentrations typical of Los Angeles. Rate laws of Erickson et al., Maahs, Hoigne et al., Penkett et al. and Martin have been compared. Reaction rate is shown in units of moles/liter-sec based on the liquid phase.

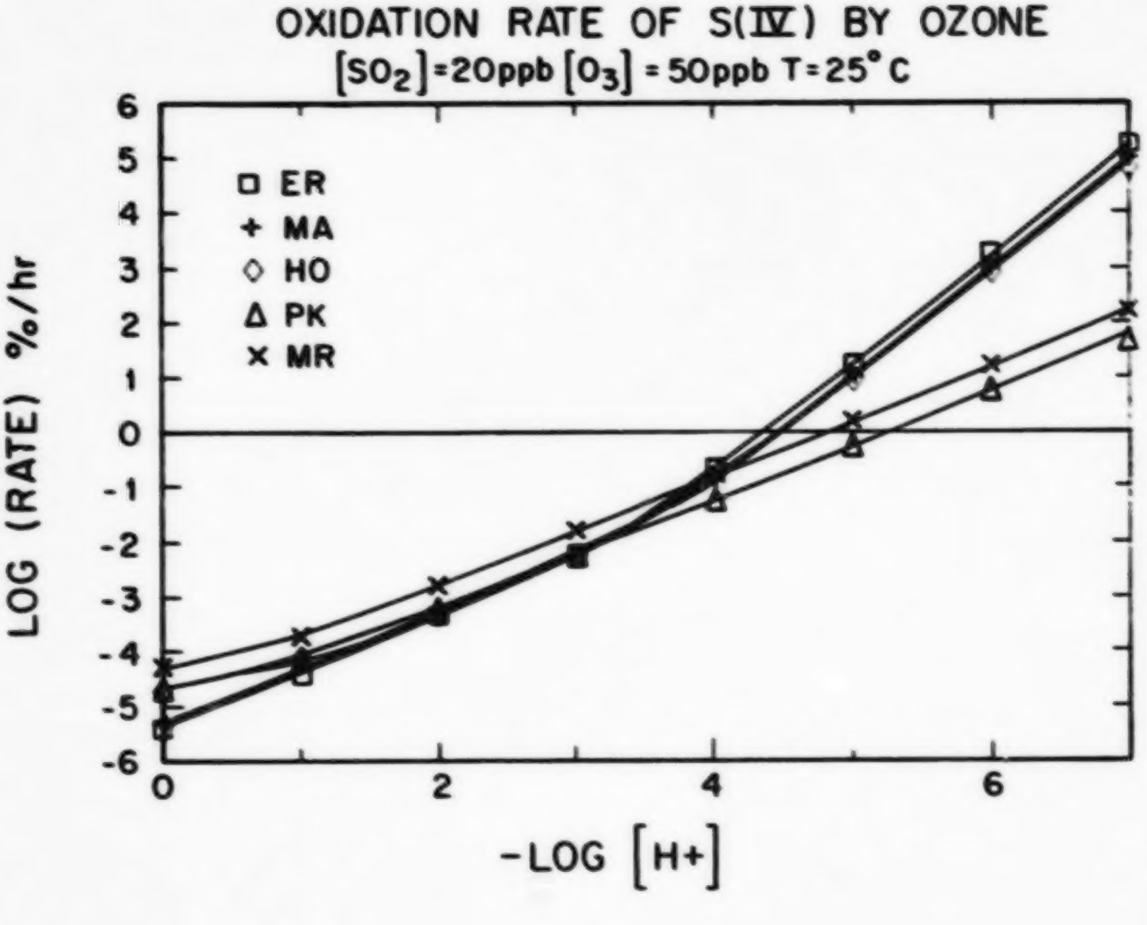


Figure 5. A comparison plot of the rate of S(IV) oxidation by ozone as a function of pH. Same conditions as for Figure 1. Reaction rates in this case are shown in units of %/hour based on the total conversion of S(IV) within a cubic meter of air.

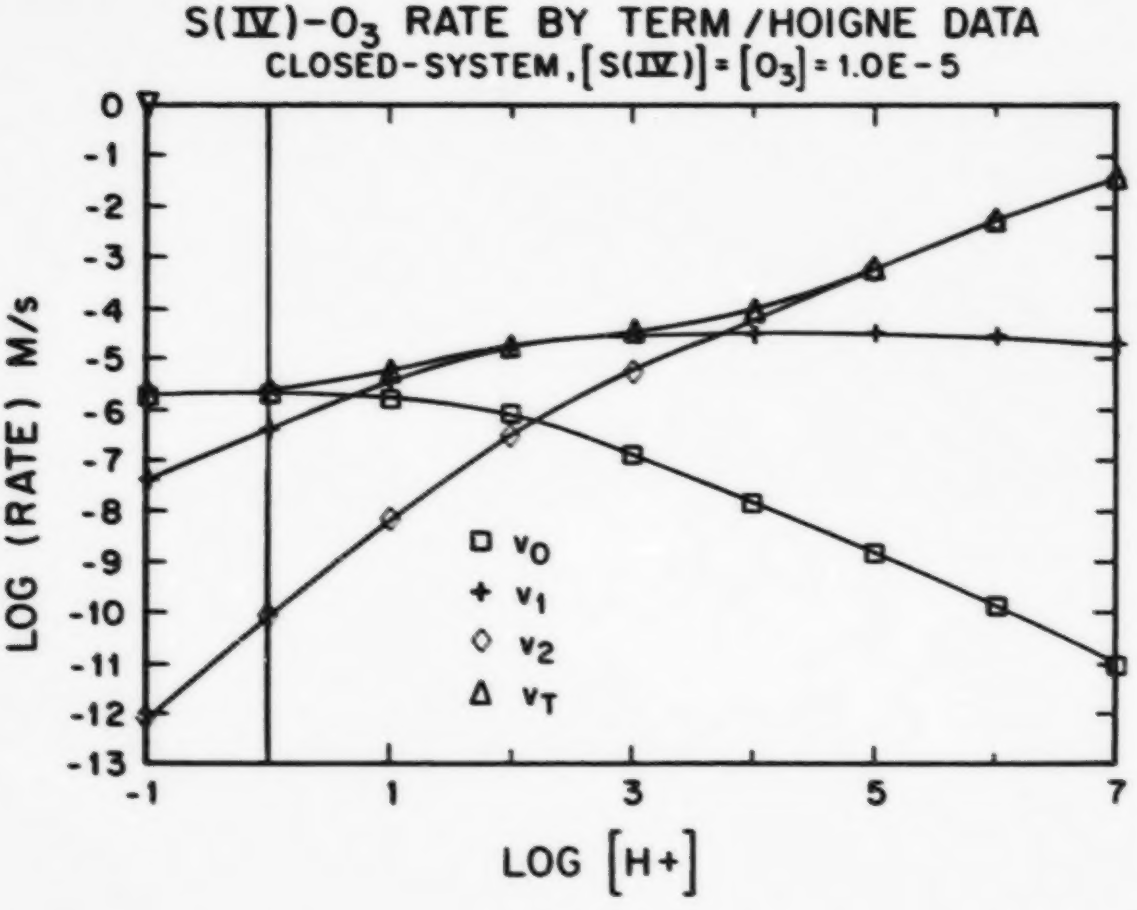


Figure 6. A plot of reaction rate versus pH for the various terms of the multi-term rate law of Hoigne et al. (1984). The total rate of conversion as given by the summation of all three terms in the rate law is indicated by $v_T$. The calculations have been made for a closed-system (i.e., no gas-phase interaction considered).

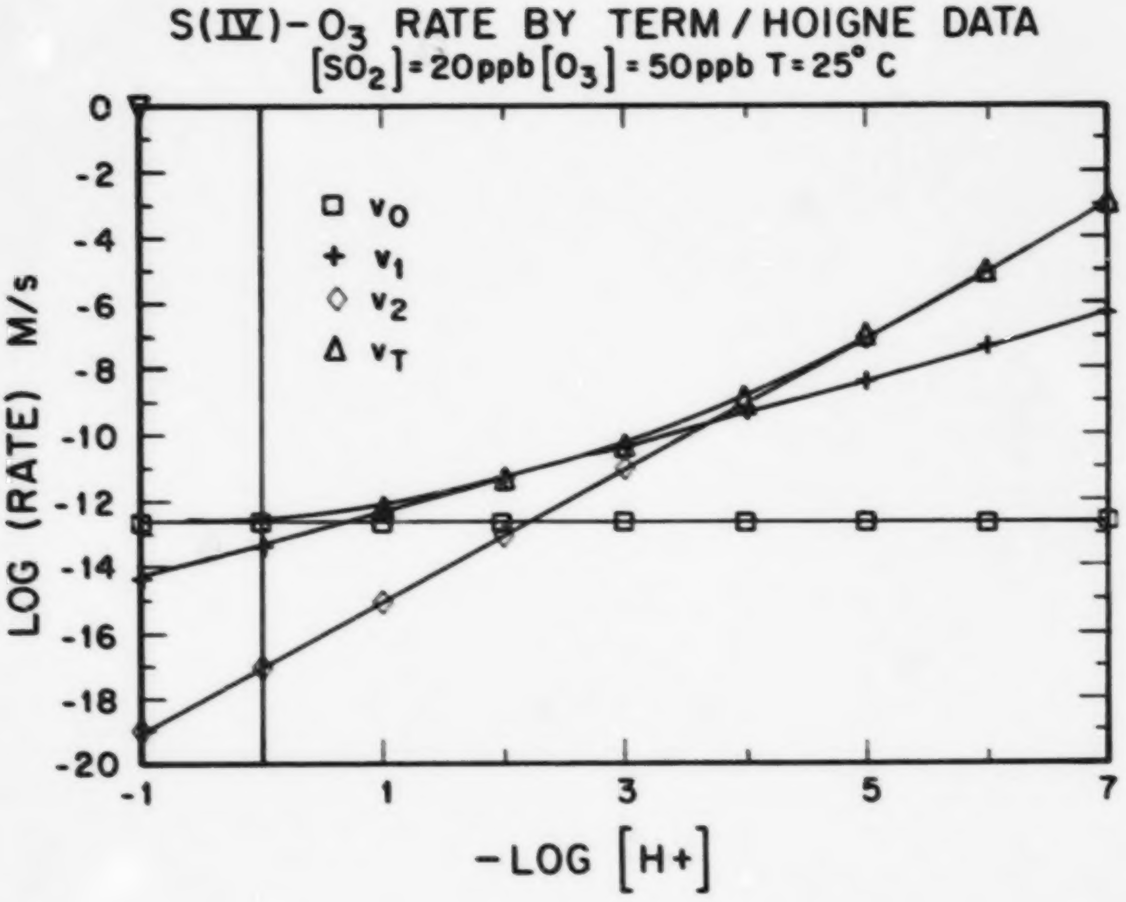


Figure 7. The same comparison as described in the caption of Figure 6 except that the system under consideration is now an open-phase system with conditions typical of the Los Angeles atmosphere.

investigators studied the kinetics of the S(IV)-ozone reaction in closed systems, this figure is most appropriate for explaining the variable $[H^+]$ dependence that is reported in Table 2. Over the pH range of 5 to 7 the slope of the log-pH plot is close to 1 (i.e., -0.89 in terms of log $[H^+]$), while over the pH range of 0 to 2 the slope is close to 0.5 (i.e., -0.45 in terms of log $[H^+]$). In the transition regime between pH 2 and 4, the slope is 0.34 (i.e., -0.34 in terms of log $[H^+]$); and finally in the extreme low pH end of the scale no pH dependency is predicted. Therefore, depending on the pH range studied by the above groups a different pH dependency may be ascertained especially over a limited pH range. Only the data of Hoigne et al. covers a sufficiently broad pH range to verify the exact pH dependency. This dependency arises because of the various alpha terms used in the overall rate equation. From a perusal of eqns. 3.2-5 under various limiting conditions, the apparent $[H^+]$ dependencies can be readily seen. From pH 5 to 7, the third term in eqn. 3.2 begins to dominate. In eqn. 3.5 the dominant term in the denominator is the $K_{a1}[H^+]$ term. This limiting case clearly gives a reciprocal first-order dependence on $[H^+]$. Over the pH range of 2 to 4, the term involving $a_1$ is dominant. The limiting condition for this case can be deduced from eqn. 3.4, which shows that two terms in the denominator are of comparable magnitude (i.e., $[H^+]^2$ and $K_{a1}[H^+]$). This will have the net effect of producing a variable, fractional and reciprocal dependence on $[H^+]$.

The contribution of each individual term in the overall rate equation is illustrated for both the open- and closed-phase systems in Figures 8 and 9. As described above the $k_2$ term is the dominant contributor to the overall rate above pH 4. Consequently, if this term

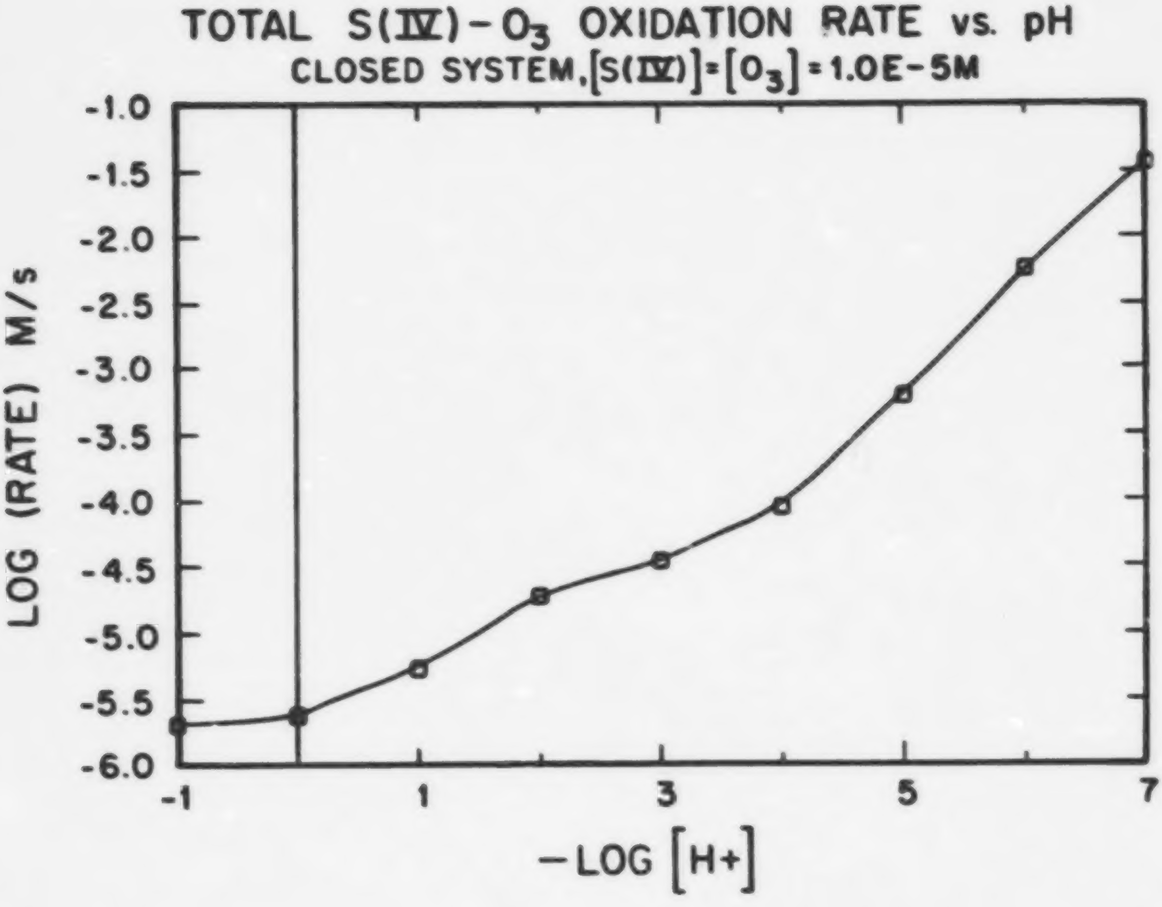


Figure 8. The total S(IV)-$O_3$ oxidation rate vs. pH using the rate law given by Hoigne et al. for a closed system. This plot helps to explain the different pH-dependencies reported by various investigators, that were in turn functions of the pH domains they chose to study.

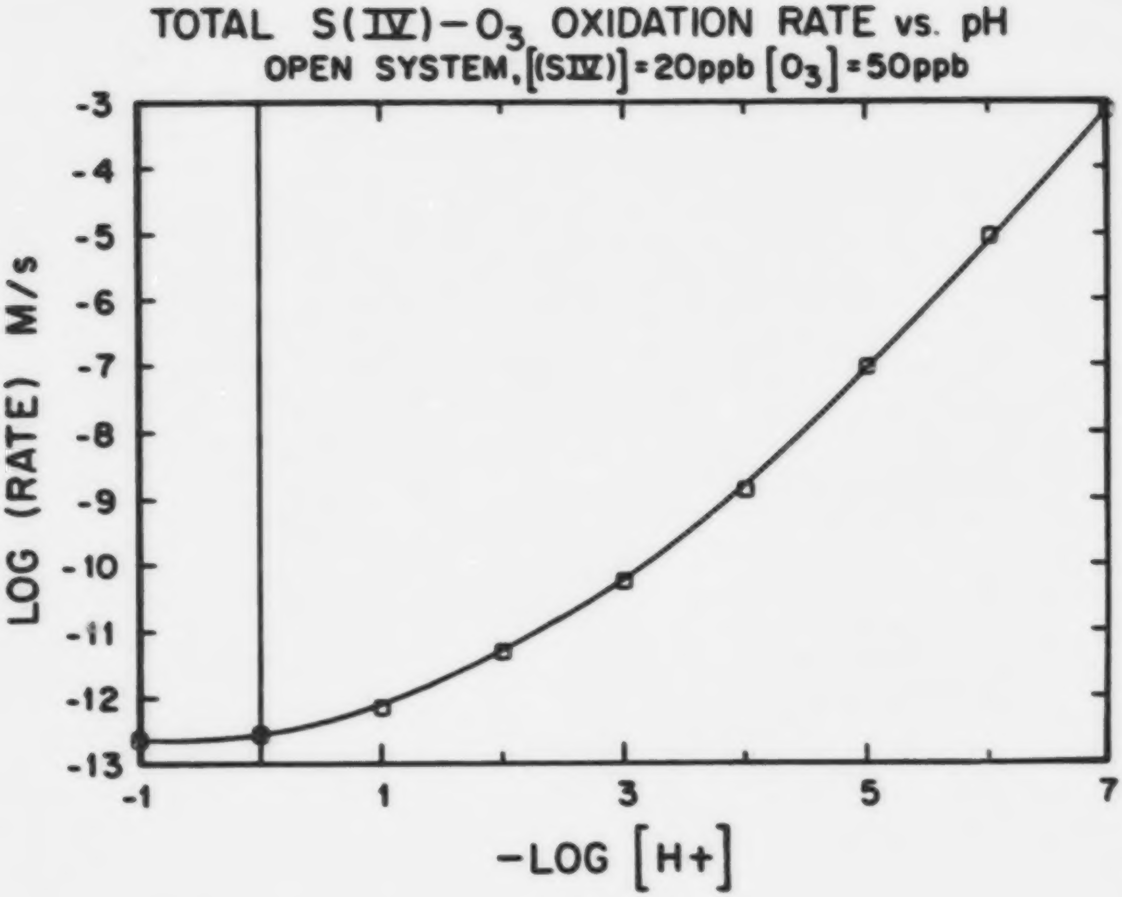
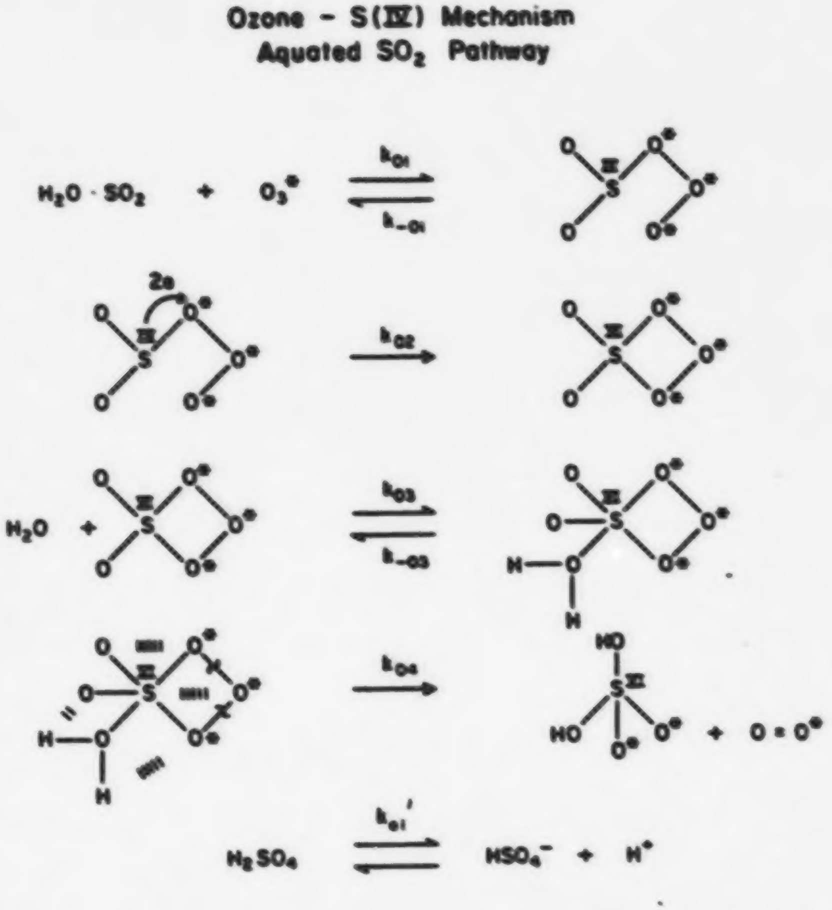


Figure 9. Same considerations as for Figure 8 except that an open-phase system was treated given conditions typical of the Los Angeles atmosphere.

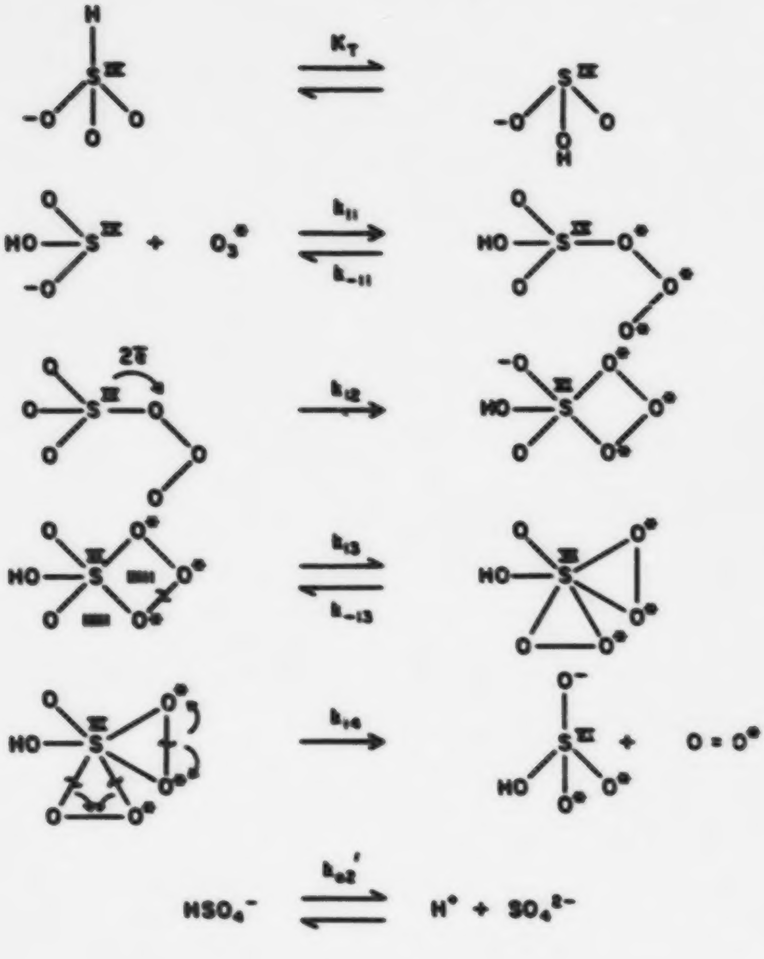
is ignored as in the case of data of Martin (1984) and Penkett et al. (1979), then the actual transformation rate will be under-predicted.

Since the rate law of eqn. 3.2 has three separate terms, there must be three individual transition states of the elemental composition given in each term, respectively (Edwards et al., 1968); and consequently, there must also be three separate mechanisms. Mechanisms consistent with the rate expression of eqn. 3.2 and with the isotopic labelling results of Espenson and Taube (1965) are given in Figures 10-12 for the kinetic terms involving $SO_3^{=}$, $HSO_3^-$, and $H_2O \cdot SO_2$, respectively. The reactions presented in Figures 10-12 may be described as polar reactions (i.e., non-radical) that proceed via an electrophilic attack of ozone on the S(IV) center of each species. The starred oxgens indicate 0-18 labelling. After electron transfer in the second step of each mechanism, a pentacoordinate sulfur intermediate is formed. The pentacoordinate-ozonide intermediate rearranges to form a hexacoordinate intermediate which subsequently breaks down to give doubly-labelled sulfate and singly-labelled oxygen. This mechanism offers a straightforward explanation for the isotopic labelling results of Espenson and Taube (1965), who have clearly shown that two 0-18 from the labelled $O_3$ are incorporated in the product sulfate. Alternatively the mechanism could be described as a nucleophilic attack by sulfur(IV) on ozone. This latter explanation is perhaps a more appropriate description in that the nucleophilic reactivity of S(IV) will increase in the order of $H_2O \cdot SO_2 < HSO_3^- < SO_3^{=}$ (Hoffmann, 1977; Hoffmann and Edwards, 1977; Edwards, 1965). Sulfate has a nucleophilic reactivity parameter, $E_n$, of 2.57 which places it just below $S^{=}$ in terms of nucleophilic strength. The corresponding value for $HSO_3^-$ is


Ozone - S(IV) Mechanism
Aquated $SO_2$ Pathway

H₂O · SO₂ + O₃*
k₀₁
k₋₀₁
2e
k₀₂
H₂O +
k₀₃
k₋₀₃
k₀₄
HO
HO
O = O*
k₀₁'
H₂SO₄
HSO₄⁻ + H⁺

Figure 10. A mechanism postulated for the first-term of the intrinsic rate expression of Table 3. In this case, the reaction proceeds simultaneously via an electrophilic attack of ozone on aquated sulfur dioxide. The *'s indicated O-18 labelled ozone. This mechanism is consistent with the results of isotopic labelling experiments of Espenson and Taube (1965).



Ozone – S(IV) Mechanism
Bisulfite Pathway

$K_T$
$k_{11}$
$k_{-11}$
$2\bar{e}$
$k_{12}$
$k_{13}$
$k_{-13}$
$k_{14}$
$k_{a2}'$
$HSO_4^-$
$H^+ + SO_4^{2-}$

Figure 11. A mechanism postulated for the second-term of the multi-term rate law for the oxidation of S(IV) by ozone. In this case, the reaction proceeds simultaneously via an electrophilic attack of ozone on bisulfite. The *'s indicated 0-18 labelled ozone. This mechanism is consistent with the results of isotopic labelling experiments of Espenson and Taube (1965).

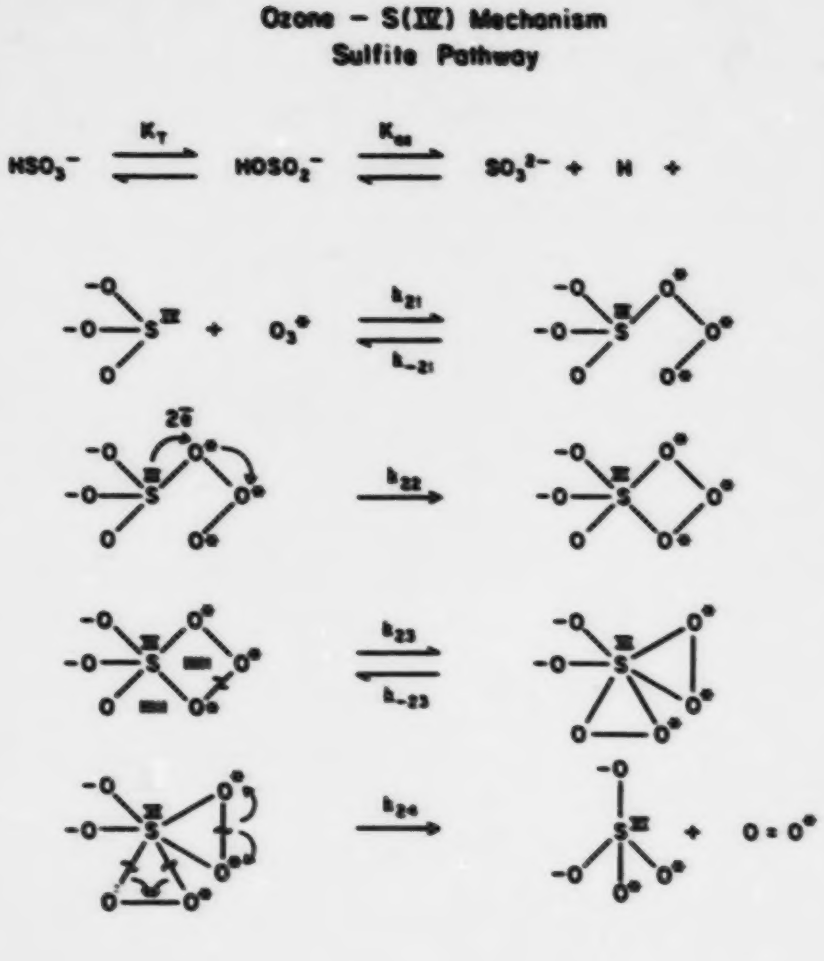

Ozone - S(IV) Mechanism
Sulfite Pathway
$K_T$
$K_a$
$HSO_3^-$
$HOSO_2^-$
$SO_3^{2-}$ + H +
$k_{21}$
$k_{-21}$
$O_3^*$
$2\bar{e}$
$k_{22}$
$k_{23}$
$k_{-23}$
$k_{24}$
O = O*

Figure 12. A mechanism postulated for the third-term of the multi-term rate law for the oxidation of S(IV) by ozone. In this case, the principal reactive form of S(IV) is sulfite. The reaction proceeds simultaneously via the electrophilic attack of ozone on sulfite. The *'s indicated O-18 labelled ozone. This mechanism is consistent with the results of isotopic labelling experiments of Espenson and Taube (1965).

substantially less (2.09). The nucleophilic reactivity on the Edwards' scale is a function of the species basicity and electrode potential (Edwards, 1965).

$$\log (k/k_0) = a \cdot E_n + B \cdot H \tag{3.11}$$

where

$$E_n = E^o + 2.6 \tag{3.12}$$

$$H = pK_a + 1.74 \tag{3.13}$$

Therefore, on this basis of nucleophilic reactivity one can predict that $SO_3^=$ should react more rapidly with $O_3$ than $HSO_3^-$ and bisulfite should react more rapidly in turn than $H_2O \cdot SO_2$. A similar relative scale of nucleophilic reactivity has been shown by Hoffmann and Edwards (1977) for nucleophilic displacements on $H_2O_2$, although the reaction of S(IV) with hydrogen peroxide is an exception. This exception will be invoked later to argue for $HOSO_2^-$ as the principal reactive bisulfite species.

The rate expressions that are derived from the mechanisms shown in Figures 10-12 are given below. They were obtained by assuming that the $k_{02}$, $k_{01}$, and $k_{02}$ are the rate-limiting steps in each mechanism and that the steady-state approximation can be applied around each respective tetrahedral S(IV)-$O_3$ adduct (i.e., intermediate).

$$v_0 = (k_{02}k_{01}/(k_{-01} + k_{02}))[H_2O \cdot SO_2][O_3] \tag{3.14}$$

$$v_1 = (k_{12}k_{11}/((k_{-11} + k_{12}))[HSO_3^-][O_3] \quad (3.15)$$

$$v_2 = (k_{22}k_{21}/(k_{-21} + k_{22}))[SO_3^=][O_3] \quad (3.16)$$

where

$$k_0 = k_{02}k_{01}/(k_{-01} + k_{02}) \quad (3.17)$$

$$k_1 = k_{12}k_{11}/(k_{-11} + k_{12}) \quad (3.18)$$

$$k_2 = k_{22}k_{21}/(k_{-21} + k_{22}) \quad (3.19)$$

and

$$v_T = v_0 + v_1 + v_2 \quad (3.20)$$

which is algebraically equivalent to eqn. 3.2.

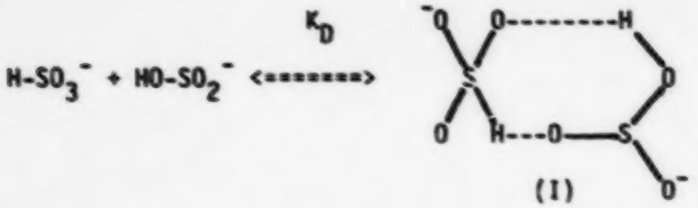
Maahs (1983b) has proposed a somewhat similar mechanism to that given in Figure 10, although he has assumed that the sulfur-hydrogen bonded sulfite is the principle reactive form of S(IV). He then used an observed positive ionic strength dependence with a slope of +1 to conclude that two monovalent, negatively charged species are reacting in the rate-limiting step of the mechanism. Therefore, he has proposed that $OH^-$ and $HSO_3^-$ react in a rate-limiting step. However, Moore and Pearson (1981) and Bunnett (1974) recommend that caution be used in the liberal application of ionic-strength dependencies for deducing a mechanism. Given the variable ionic-strength dependence as a function of pH as observed by Maahs (Maahs' Fig. 4), a more likely explanation for the observed dependence is a secondary ionic-strength effect in which the values of $K_{a1}$ and $K_{a2}$ are being shifted dramatically downward as the ionic strength is increased. For example at $u = 0$, $pK_{a2} = 7.22$ while at $u = 1.0$ the same constant is 6.34. The net effect of this upward shift in $K_{a2}$ is to increase the relative fraction of $SO_3^=$ at the same pH and consequently to increase the apparent overall rate of reaction because of an increased contribution by the $k_2$ term. Therefore, at pH 5 Maahs should in fact have seen a slope of approximately one in his Davies' equation plot (Maahs' Fig. 4). However, as he shifted the pH downward to 3.0 the relative contribution of the $k_2$ term diminishes and the apparent rate is then controlled by the $k_1$ term which is more critically dependent on the value of $K_{a1}$. The value of $K_{a1}$ varies from 1.89 at $u = 0$ to 1.37 at $u = 1.0$. At pH 3 the apparent increase in rate with an increase in ionic strength is due to the combined effect of upward shifts in both $K_{a1}$ and $K_{a1}$, however, a Davies' plot slope of less than one would be expected. Maahs reports a slope of 0.7 at pH 3.1. I would interpret this preferentially in terms of a secondary ionic strength effect rather than a primary effect as concluded by Maahs.

Furthermore, I have to question Maahs' assertion that the $H\text{-}SO_3^-$ form of bisulfite is the predominant tautomer as opposed to the $HO\text{-}SO_2^-$ form. He cites the work of Guthrie (1978) in support of his contention that $H\text{-}SO_3^-$ is predominant with $[H\text{-}SO_3^-]/[HO\text{-}SO_2^-] = 40$. Guthrie's conclusions were drawn on the basis of the Linear Free Energy Relationship (LFER) between dimethyl sulfite and aquated sulfur dioxide ($H_2O \cdot SO_2$). Care must be exerted when constructing a LFER among species that do not constitute an obvious homologous series (Edwards, 1965). Many assumptions go into the construction of a LFER. One of the critical ones is that the entropy changes for a homologous series of compounds is constant. This assumption most likely will not hold for $(CH_3O)_2SO$ and $H_2O \cdot SO_2$ which differ dramatically in terms of their polarity (i.e., the entropy of solvation should not be the same for both). Cotton and Wilkinson (1981) claim that there is no conclusive evidence for the existence of a tautomeric equilibrium as shown in eqn. 3.21.

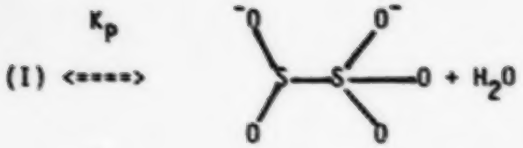
$$HO\text{-}SO_2^- \Longleftrightarrow H\text{-}SO_3^- \qquad (3.21)$$

Stromberg et al. (1983) have concluded that $HO\text{-}SO_2^-$ is the more stable tautomer by 16 kJ/mol based on _ab initio_ calculations. However, they are cautious to state that in aqueous solution both most likely will coexist in approximately equal proportions. Golding (1960) has argued that both species coexist in solution but that $HO\text{-}SO_3^-$ dominates the UV spectrum of S(IV) due to its single empty pi-orbital and greater oscillator strength for the first electronic transition. He concluded that at low concentrations (i.e., $[S(IV)] \leq 10^{-3}$ M) the $HO\text{-}SO_2^-$ species predominates. At higher concentrations the two bisulfite tautomers form a dimer which eventually dehydrates to form pyrosulfite, $S_2O_5^{2-}$ as shown below:

$$HO\text{-}SO_2^- \overset{K_T}{\Longleftrightarrow} H\text{-}SO_3^- \qquad (3.22)$$



(3.23)



(3.24)

Recent Raman and UV measurements by Connick et al. (1982) substantiate Golding's arguments for the coexistence of both tautomers in aqueous solution. In addition, they determined that overall pyrosulfite formation constant, $K_P^1$ ($K_P^1 = K_TK_DK_P$) is 0.088 $M^{-1}$ as compared to Golding's value of 0.07 $M^{-1}$ at ionic strength of 0.1 M and Bourne et al. (1974)'s value of 0.115 at the same ionic strength. Recently, Rhee and Dasgupta (1984) have determined an overall dimerization constant, $K_D^1$ ($K_D^1 = K_TK_D$) of $1.75 \times 10^3$ $M^{-1}$ at 25°C. Theoretical work of Meyer et al. (1976) and Baird and Taylor (1981) suggests that the H-S bonded tautomer is the most energetically favorable. However, Stromberg et al. (1983) argue that the latter two papers lack computational rigor and therefore their conclusions are suspect.

The chemical reactivity of bisulfite can be best explained in terms of the $HO\text{-}SO_2^-$ tautomer as the predominant species provided that the two tautomers are in rapid equilibrium. For example, the kinetics and mechanism of the hydrogen peroxide-bisulfite reaction, which occurs via a nucleophilic attack by hydrogen peroxide on bisulfite, suggest that the pyramidal, $HO\text{-}SO_2^-$ form would provide a stereochemically more tractive site for attack by a nucleophile than the tetrahedral tautomer. The latter would clearly be more sterically hindered and consequently require a higher activation energy. Likewise, the electrophilic attack of ozone on the pyramidal HO-S form of bisulfite should be more facile than attack on the tetrahedral H-S bonded form.

## D. CONCLUSIONS

Kinetic data obtained from a number of different investigators on the reaction of S(IV) with ozone in aqueous solution has been analyzed in terms of a single self-consistent rate expression. The rate expression that most appropriately fits all kinetic observations treated in this study is:

$$-d[S(IV)]/dt = (k_0a_0 + k_1a_1 + k_2a_2)[S(IV)][O_3]$$

where

$$a_0 = [H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

$$a_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

$$a_2 = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$$

This kinetic expression is similar in form to the empirical rate laws reported by Erickson et al. (1977) and Hoigne et al. (1984). The recommended values for $k_0$, $k_1$, and $k_2$ are $(2.4 \pm 1.1) \times 10^4$ $M^{-1}s^{-1}$, $(3.7 \pm 0.7) \times 10^5$ $M^{-1}s^{-1}$, and $(1.5 \pm 0.6) \times 10^9$ $M^{-1}s^{-1}$, respectively. The activation energies that are recommended for $k_1$ and $k_2$ are taken from Erickson et al. (1977) as 46.0 kJ/mol and 43.9 kJ/mol, respectively. The reaction proceeds via three independent pathways that involve an nucleophilic attack on ozone by $SO_3^{=}$, $HO\text{-}SO_2^{-}$, and $SO_2 \cdot H_2O$. Arguments for the existence of $HO\text{-}SO_2^{-}$ as the predominant form of bisulfite in aqueous solution are presented. Rate laws and kinetic data of five investigators are compared for an open cloud water system with a liquid water content of 0.2 $gm/^3$.

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# APPENDIX A: KINETIC DATA

# FOR AQUEOUS-PHASE REACTIONS

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH;
## BIMOLECULAR REACTIONS OF INORGANIC SPECIES
### TABLE K1

| Reaction | pH | k ($M^{-1}s^{-1}$) | Reference |
|---|---|---|---|
| $OH + OH \rightarrow H_2O_2$ | 0.4 | $(4 \pm 1) \times 10^9$ | Farhataziz & Ross (1977) |
| | 3.0 | $6 \times 10^9$ | Farhataziz & Ross (1977) |
| | 3.7 | $(5.2 \pm 0.7) \times 10^9$ | Farhataziz & Ross (1977) |
| | 7.0 | $(4 \pm 1) \times 10^9$ | Farhataziz & Ross (1977) |
| | 7.0 | $(5.2 \pm 0.5) \times 10^9$ | Farhataziz & Ross (1977) |
| I $OH + HO_2 \rightarrow H_2O_3$ | 0.8 | $1.4 \times 10^{10}$ | Farhataziz & Ross (1977) |
| II $OH + HO_2 \rightarrow H_2O + O_2$ | >2 | $6 \times 10^9$ | Farhataziz & Ross (1977) |
| | 3.0 | $1.5 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 7.0 | $3.0 \times 10^9$ | Farhataziz & Ross (1977) |
| | $k_I/k_{II}$ | 2.3 | Farhataziz & Ross (1977) |
| $SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + H^+ + CO_3^-$ | | | Ross & Neta (1978) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
## TABLE K2

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $OH + HCO_3^- \rightarrow H_2O + CO_3^-$ | 6.5 | $1.0 \times 10^7$ | Farhataziz & Ross (1977) |
| | 8.4 | $1.5 \times 10^7$ | Farhataziz & Ross (1977) |
| $OH + CO_3^{2-} \rightarrow OH^- + CO_3^-$ | 10.5 | $4.5 \times 10^8$ | Farhataziz & Ross (1977) |
| | 10.6 | $(4.0 \pm 0.2) \times 10^8$ | Farhataziz & Ross (1977) |
| | 11.0 | $3.8 \times 10^8$ | Farhataziz & Ross (1977) |
| | 11.0 | $3.5 \times 10^8$ | Farhataziz & Ross (1977) |
| | 11.0 | $3.65 \times 10^8$ | Farhataziz & Ross (1977) |
| (I) $OH + Cl^- \rightleftharpoons ClOH^-$ | 1-2.5 | $8.9 \times 10^7 - 6.4 \times 10^8$ | Farhataziz & Ross (1977) |
| (II) $ClOH^- + H^+ \rightleftharpoons Cl + H_2O$ | 1-2.7 | $6.7 \times 10^7 - 1.6 \times 10^9$ | Farhataziz & Ross (1977) |
| (III) $Cl + Cl \rightleftharpoons Cl_2^-$ | 1-3 | $1.16 \times 10^{10} - 2.16 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 0-3 | $0.32 \times 10^{10} - 1.84 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 1-3 | $1.0 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 2 | $5.2 \times 10^8$ | Farhataziz & Ross (1977) |
| | 0.8-3.4 | $1.5 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 2 | $4.3 \times 10^9$ (I)<br>$2.1 \times 10^{10}$ (II)<br>$2.1 \times 10^{10}$ (III) | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
## TABLE K3

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $OH + H_2O_2 \rightarrow HO_2 + H_2O$ | 3 | $1.2 \times 10^7$ | Farhataziz & Ross (1977) |
| | 6 | $4.5 \times 10^7$ | Farhataziz & Ross (1977) |
| | 7 | $(2.6 \pm 0.8) \times 10^7$ | Farhataziz & Ross (1977) |
| | 8.4 | $6.5 \times 10^7$ | Farhataziz & Ross (1977) |
| | | $2.7 \times 10^7$ | Christensen (1978) |
| $I^- + OH \rightarrow HOI^-$ | 0-2 | $1.6 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $HOI^- \rightarrow OH^- + I$ | 2 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $I + I^- \rightleftharpoons I_2^-$ | 3-5.5 | $7.4 \times 10^9$ | Farhataziz & Ross (1977) |
| | 5.5 | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 6 | $1.4 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 7 | $(1.02 \pm 0.13) \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 7 | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 7 | $1.8 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 9 | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
## TABLE K4

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $OH + O_2^- \rightarrow OH^- + O_2$ | 2.74-6.75 | $1.01 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 7 | $(8.0 \pm 1) \times 10^9$ | Farhataziz & Ross (1977) |
| $OH + Br^- \rightleftharpoons BrOH$ | | | |
| $BrOH^- \rightleftharpoons Br + OH^-$ | | | |
| $Br + Br^- \rightleftharpoons Br_2^-$ | | | |
| $BrOH^- + Br^- \rightleftharpoons Br_2^- + OH^-$ | | | |
| | 0.8 | $1.6 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 1.3 | $1.0 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 1.3 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 2.0 | $3.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 2.7 | $8.1 \times 10^9$ | Farhataziz & Ross (1977) |
| | 3.0 | $5.0 \times 10^9$ | Farhataziz & Ross (1977) |
| | 5.5 | $1.2 \times 10^9$ | Farhataziz & Ross (1977) |
| | 6.0 | $1.2 \times 10^9$ | Farhataziz & Ross (1977) |
| | 7.0 | $3.9 \times 10^9$ | Farhataziz & Ross (1977) |
| | 7.0 | $1.0 \times 10^9$ | Farhataziz & Ross (1977) |
| | 1-7 | $(1.06 \pm 0.08) \times 10^{10}$ | Farhataziz & Ross (1977) |

### KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
### TABLE K5

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $OH + Cu^{2+} \rightarrow Cu^{3+} + OH^-$ | 3-6 | $(3.1 \pm 0.3) \times 10^8$ | Farhataziz & Ross (1977) |
| $OH + Cu^{2+} \rightarrow CuOH^{2+}$ | 5 | $3 \times 10^8$ | Farhataziz & Ross (1977) |
| $CuOH^+ + OH \rightarrow Cu(OH)_2^+$ | 5.7 | $(3.1 \pm 0.3) \times 10^8$ | Farhataziz & Ross (1977) |
|  | 7 | $3.5 \times 10^8$ | Farhataziz & Ross (1977) |
|  | ? | $3.5 \times 10^8$ | Farhataziz & Ross (1977) |
|  | ? | $3.5 \times 10^8$ | Farhataziz & Ross (1977) |
| $OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ | 0.4 | $1.7 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 0.8 | $1.2 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 1.0 | $(2.3 \pm 0.2) \times 10^8$ | Farhataziz & Ross (1977) |
|  | 2.0 | $5.0 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 3.5 | $(5 \pm 1) \times 10^8$ | Farhataziz & Ross (1977) |
|  | 4.5-6.2 | $3.4 \times 10^8$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES

## TABLE K6

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $Mn^{2+} + OH \rightarrow Mn^{3+} + OH^-$ | ? | $\geq 1.4 \times 10^8$ | Farhataziz & Ross (1977) |
| $OH + NH_3 \rightarrow H_2O + NH_2$ | ? | $1.0 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 11.3 | $3.6 \times 10^7$ | Farhataziz & Ross (1977) |
| $NH_2 + OH \rightarrow NH_2OH$ | ? | $9.5 \times 10^9$ | Farhataziz & Ross (1977) |
| $NH_2OH + OH \rightarrow$ | 8 | $9.5 \times 10^9$ | Farhataziz & Ross (1977) |
| $NOH(SO_3)_2^{2-} + OH \rightarrow H_2O + ON(SO_3)_2^{2-}$ | 8.4-12 | $5.7 \times 10^8$ | Farhataziz & Ross (1977) |
| $ON(SO_3)_2^{2-} + OH \rightarrow$ | ? | $2.6 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $OH + NO \rightarrow NO_2^- + H^+$ | 7 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
|  | 7 | $8.9 \times 10^{10}$ | Farhataziz & Ross (1977) |
|  | 7 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
|  | 7 | $1.0 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $OH + NO_2 \rightarrow HO_2NO$ | 9 | $1.3 \times 10^9$ | Farhataziz & Ross (1977) |
| $HNO_2 + OH \rightarrow NO_2 + H_2O$ |  | $1.0 \times 10^9$ | Rettich (1978) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES

## TABLE K7

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $OH + NO_2^- \rightarrow NO_2 + OH^-$ | 9 | $8.1 \times 10^9$ | Farhataziz & Ross (1977) |
| | 9 | $7.1 \times 10^9$ | Farhataziz & Ross (1977) |
| | 9 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 10.7 | $6.6 \times 10^9$ | Farhataziz & Ross (1977) |
| | ? | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | ? | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $NO_3^- + OH \rightarrow OH^- + NO_3$ | 9 | $<5 \times 10^5$ | Farhataziz & Ross (1977) |
| $H_3PO_4 + OH \rightarrow H_2O + H_2PO_4$ | 0 | $2.6 \times 10^6$ | Farhataziz & Ross (1977) |
| $H_2PO_4^- + OH \rightarrow H_2PO_4 + OH^-$ | 3.8-4.0 | $2.2 \times 10^6$ | Farhataziz & Ross (1977) |
| $HPO_4^{2-} + OH \rightarrow$ | 9 -12.3 | $(7.9 \pm 0.4) \times 10^5$ | Farhataziz & Ross (1977) |
| $H_2S + OH \rightarrow H_2O + HS$ | 2 - 5.7 | $2.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 5.5 | $1.5 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 6 | $1.9 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 6 | $1.4 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $HS^- + OH \rightarrow OH^- + SH$ | 10.5 | $9.4 \times 10^9$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
## TABLE K8

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $HSO_4^- + OH \rightarrow HSO_4 + OH^-$ | 0.3-2 | $1.2 \times 10^6$ | Farhataziz & Ross (1977) |
| $HSO_4^- + OH \rightarrow SO_4^- + H_2O$ | 4M $H^+$ | $1.5 \times 10^6$ | Farhataziz & Ross (1977) |
|  | 7 | $6.9 \times 10^5$ | Farhataziz & Ross (1977) |
|  | 7 | $1.6 \times 10^6$ | Farhataziz & Ross (1977) |
| $OH + S_2O_3^{2-} \rightarrow S_2O_3^- + OH^-$ | ? | $1.2 \times 10^9$ | Farhataziz & Ross (1977) |
|  | ? | $3.0 \times 10^9$ | Farhataziz & Ross (1977) |
|  | ? | $1.6 \times 10^9$ | Farhataziz & Ross (1977) |
|  | ? | $8.0 \times 10^9$ | Farhataziz & Ross (1977) |
| $OH + HSO_5^- \rightarrow SO_5^- + H_2O$ |  |  |  |
| $OH + HSO_5^- \rightarrow HSO_5^- + OH^-$ | ? | $3.5 \times 10^8$ | Farhataziz & Ross (1977) |
| $OH + Zn^{2+} \rightarrow Zn^{3+} + OH^-$ | ? | $< 5 \times 10^5$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES

### TABLE K9

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $CH_2 = CHCHO + HO \rightarrow$ adduct<br>(acrolein) | ? | $7.0 \times 10^9$ | Farhataziz & Ross (1977) |
| $CH_2 = CHCONH_2 + HO \rightarrow$ adduct<br>(acrylamide) | 7 | $4.1 \times 10^9$ | Farhataziz & Ross (1977) |
| | 5.6 | $4.7 \times 10^9$ | Farhataziz & Ross (1977) |
| $CH_2 = CHCO_2H + OH \rightarrow$<br>(acrylic acid) | 1 | $1.4 \times 10^9$ | Farhataziz & Ross (1977) |
| $HO_2C(CH_2)_4\ CO_2H + OH \rightarrow$<br>(adipic acid) | 1 | $2.9 \times 10^8$ | Farhataziz & Ross (1977) |
| | 2-2.2 | $1.7 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_6H_5NH_2 + OH \rightarrow C_6H_5NH + H_2O$<br>(aniline) | 7.5-9 | $2.9 \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 9 | $8.9 \times 10^9$ | |
| $C_6H_5OCH_3 + OH \rightarrow (HO)C_6H_5OCH_3$<br>(anisole) | 7 | $(1.2 \pm 3) \times 10^{10}$ | Farhataziz & Ross (1977) |
| | 9 | $6 \times 10^9$ | Farhataziz & Ross (1977) |
| | 9 | $5.7 \times 10^9$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES

### TABLE K10

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $CH_3CHO + OH \rightarrow$ | 1 | $5 \times 10^8$ | Farhataziz & Ross (1977) |
| $CH_3CONH_2 + OH \rightarrow CH_2CONH_2 + H_2O$ | 5.5 | $1.9 \times 10^8$ | Farhataziz & Ross (1977) |
| $OH + CH_3CONH_2 \rightarrow H_2O + CH_3CONH$ | 9.0 | $1.3 \times 10^7$ | Farhataziz & Ross (1977) |
| (acetamide) | ? | $1.9 \times 10^8$ | Farhataziz & Ross (1977) |
| $CH_3CO_2^- + OH \rightarrow CH_2CO_2^- + H_2O$ | 5.6 | $7.0 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 9.0 | $8.8 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 9.0 | $7.2 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 10.7 | $6.3 \times 10^7$ | Farhataziz & Ross (1977) |
| $CH_3CO_2H + OH \rightarrow CH_2CO_2H + H_2O$ | 1 | $1.8 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 1 | $2.3 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 1 | $2.0 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 1 | $2.0 \times 10^7$ | Farhataziz & Ross (1977) |
| $CH_3COCH_3 + OH \rightarrow CH_2COCH_3 + H_2O$ | 0.8 | $3.8 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 1 | $7.2 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 2-2.2 | $7.6 \times 10^7$ | Farhataziz & Ross (1977) |
|  | 7 | $9.0 \times 10^7$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K11

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $C_6H_5CHO + OH \rightarrow$ | 9 | $4.4 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_6H_6 + OH \rightarrow C_6H_6OH$ | 1 | $7.4 \times 10^8$ | Farhataziz & Ross (1977) |
| | 1.2 | $4.8 \times 10^9$ | Farhataziz & Ross (1977) |
| | 2-2.2 | $5.4 \times 10^9$ | Farhataziz & Ross (1977) |
| | 3 | $6.3 \times 10^9$ | Farhataziz & Ross (1977) |
| | 6-7 | $5 \times 10^9$ | Farhataziz & Ross (1977) |
| | 7 | $7.8 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_6H_5SO_3H + OH \rightarrow (HO)C_6H_5SO_3H$ | 1 | $1.1 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_6H_5SO_3^- + OH \rightarrow (HO)C_6H_5SO_3^-$ (benzenesulfonate) | 7 | $(4.7 \pm 0.6) \times 10^9$ | Farhataziz & Ross (1977) |
| $C_6H_5CO_2H + OH \rightarrow (HO)C_6H_5CO_2H$ | 1 | $1.6 \times 10^9$ | Farhataziz & Ross (1977) |
| | 3 | $(2.1 \pm 0.3) \times 10^9$ | Farhataziz & Ross (1977) |
| $C_4H_9OH + OH \rightarrow H_2O + C_3H_7CHOH$ | 2-2.2 | $4.6 \times 10^9$ | Farhataziz & Ross (1977) |
| | 5-5.5 | $4.6 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_3H_7CHO + OH \rightarrow$ | 2.0 | $3.8 \times 10^9$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES

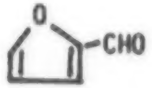
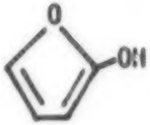
### TABLE K12

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $C_3H_7CO_2H + OH \rightarrow$ | 1 | $1.6 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 2-2.2 | $1.9 \times 10^9$ | Farhataziz & Ross (1977) |
| $CS_2 + OH \rightarrow CS_2OH$ | 7.6 | $8.0 \times 10^9$ | Farhataziz & Ross (1977) |
| $CS_2OH \rightleftharpoons CSO^- + H^+$ |  |  |  |
| $O\text{-}CH_3\phi\text{-}OH + OH \rightarrow$ | 9 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| o-cresol |  |  |  |
| $p\text{-}CH_3\phi\text{-}OH + OH \rightarrow$ | 9 | $1.3 \times 10^{10}$ | Farhataziz & Ross (1977) |
|  | 5.5 | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $CH_3CH = CCHO + OH \rightarrow$ | ? | $5.8 \times 10^9$ | Farhataziz & Ross (1977) |
| $CH_3CH = CCO_2H + OH \rightarrow$ (crotonic acid) | 1 | $2.7 \times 10^9$ | Farhataziz & Ross (1977) |
| $(CH_3)_2S = O + OH \rightarrow$ (dimethyl sulfoxide) | ? | $7.0 \times 10^9$ | Farhataziz & Ross (1977) |
| $(CH_3)_2SO_2 + OH \rightarrow$ | 1.5 | $< 6 \times 10^6$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K13

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $C_2H_5OH + OH \rightarrow H_2O + CH_3CHOH$ | 1 | $1.9 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_2H_5OH + OH \rightarrow H_2O + CH_2CH_2OH$ | 2 | $1.65 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_2H_5OH + OH \rightarrow H_2O + CH_3CH_2O$ | 2-2.2 | $2.0 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 3 | $1.6 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 5.5 | $1.7 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 5-5.5 | $1.8 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 7 | $1.8 \times 10^9$ | Farhataziz & Ross (1977) |
| $C_2H_5CO_2CH_3 + OH \rightarrow$ | 1 | $2.5 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 2.0-2.2 | $2.8 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 6-7 | $4.0 \times 10^8$ | Farhataziz & Ross (1977) |
| $HCO_2C_2H_5 + OH \rightarrow$ | 6-7 | $3.8 \times 10^8$ | Farhataziz & Ross (1977) |
| $HCHO + OH \rightarrow H_2O + CHO$ | 1.0 | $6.9 \times 10^8$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K14

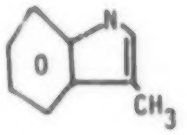
| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $HCOO^- + OH \rightarrow H_2O + COO^-$ | 5.8-10.1 | $1.9 \times 10^9$ | Farhataziz & Ross (1977) |
| | 2-5 | $3.4 \times 10^9$ | Farhataziz & Ross (1977) |
| | 7 | $2.9 \times 10^9$ | Farhataziz & Ross (1977) |
| | 6.98 | $2.9 \times 10^9$ | Farhataziz & Ross (1977) |
| | 8.4 | $2.9 \times 10^9$ | Farhataziz & Ross (1977) |
| $HCOOH + OH \rightarrow H_2O + COOH$ | 1 | $1.5 \times 10^8$ | Farhataziz & Ross (1977) |
| | 1 | $1.5 \times 10^8$ | Farhataziz & Ross (1977) |
| | 1 | $1.6 \times 10^8$ | Farhataziz & Ross (1977) |
| | 2-5 | $1.6 \times 10^8$ | Farhataziz & Ross (1977) |
| $HO_2CCH = CHCO_2H + OH \rightarrow$<br>trans-butenedioic acid | 1 | $1.1 \times 10^9$ | Farhataziz & Ross (1977) |
|  + OH<br>furaldehyde | 9 | $7.75 \times 10^9$ | Farhataziz & Ross (1977) |
|  + OH → | 9 | $1.5 \times 10^{10}$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K15

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $HOCH_2CO_2H$<br>(glycolic acid) | 1 | $4.6 \times 10^8$ | Farhataziz & Ross (1977) |
| | 2-2.2 | $4.6 \times 10^8$ | Farhataziz & Ross (1977) |
| $HOCH_2CO_2^-$ | 5.5 | $(8.6 \pm 0.7) \times 10^8$ | Farhataziz & Ross (1977) |
| $m\text{-}\phi\text{-}(OH)_2$ | 9 | $1.2 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $p\text{-}\phi\text{-}(OH)_2$ | 9 | $1.1 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $CH_3\overset{OH}{C}HCO_2H$ | 1 | $3.9 \times 10^8$ | Farhataziz & Ross (1977) |
| | 1 | $4.3 \times 10^8$ | Farhataziz & Ross (1977) |
| | 2-2.2 | $6.5 \times 10^8$ | Farhataziz & Ross (1977) |
| $HO_2CCH_2CO_2H$<br>(malonic acid) | 1 | $2.6 \times 10^7$ | Farhataziz & Ross (1977) |
| | 2-2.2 | $2.0 \times 10^7$ | Farhataziz & Ross (1977) |
| $^-O_2CCH_2CO_2^-$ | 9 | $5.5 \times 10^7$ | Farhataziz & Ross (1977) |
| $CH_4 + OH \rightarrow H_2O + CH_3$ | 9 | $2.4 \times 10^8$ | Farhataziz & Ross (1977) |
| | 5.5 | $1.2 \times 10^8$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES

## TABLE K16

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $CH_3SO_3H + OH \rightarrow$ | 2 | $1.3 \times 10^9$ | Farhataziz & Ross (1977) |
| $CH_3SH + OH \rightarrow H_2O + CH_3S$ | 7 | $3.3 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $CH_3OH + OH \rightarrow H_2O + CH_2OH$ | 1 | $1.1 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 2 | $2.8 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 2-2.2 | $8.6 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 4.5 | $3 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 5-5.5 | $9.4 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 6 | $8.6 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 7 | $8.8 \times 10^8$ | Farhataziz & Ross (1977) |
|  $+ OH \rightarrow$ | 9 | $(1.05 \pm 0.09) \times 10^{10}$ | Farhataziz & Ross (1977) |
| $CH_3CO_2CH_3$ | 1 | $2 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 2 | $1.3 \times 10^8$ | Farhataziz & Ross (1977) |
|  | 6-7 | $1.2 \times 10^8$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
### TABLE K17

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $CH_3NH_2 + OH \rightarrow H_2O + CH_2NH_2$ | 10.5 | $1.8 \times 10^9$ | Farhataziz & Ross (1977) |
| | 11.1 | $3.3 \times 10^9$ | Farhataziz & Ross (1977) |
| | 11.5-12.5 | $4.7 \times 10^9$ | Farhataziz & Ross (1977) |
| $(CH_3)_2S + OH \rightarrow CH_3S(OH)CH_3$<br>$\rightarrow CH_3SCH_3^+ + OH^-$ | ? | $5.2 \times 10^9$ | Farhataziz & Ross (1977) |
| $\phi\text{-}NO_2 + OH \rightarrow HOC_6H_5NO_2$ | 1 | $6.7 \times 10^8$ | Farhataziz & Ross (1977) |
| | 7 | $3.2 \times 10^9$ | Farhataziz & Ross (1977) |
| | 9 | $3.3 \times 10^9$ | Farhataziz & Ross (1977) |
| $p\text{-}NO_2\text{-}\phi\text{-}OH + OH \rightarrow$ | 2 | $3.8 \times 10^9$ | Farhataziz & Ross (1977) |
| $o\text{-}NO_2\text{-}\phi\text{-}OH + OH \rightarrow$ | 9 | $9.2 \times 10^9$ | Farhataziz & Ross (1977) |
| $(COOH)_2 + OH \rightarrow H_2O+CO_2+CO_2H$ | 2-2.5 | $9.2 \times 10^6$ | Farhataziz & Ross (1977) |
| $HC_2O_4^- + OH \rightarrow OH + CO_2 + CO_2H$ | 2.7 | $5.6 \times 10^8$ | Farhataziz & Ross (1977) |
| $C_2O_4^{2-} + OH \rightarrow CO_2 + CO_2^- + OH^-$ | 7 | $1.0 \times 10^7$ | Farhataziz & Ross (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K18

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $\phi$-OH + OH → $C_6H_5(OH)_2$ | 1.2 | $9.7 \times 10^9$ | Farhataziz & Ross (1977) |
|  | 6-7 | $1.8 \times 10^{10}$ | Farhataziz & Ross (1977) |
|  | 7.4-7.7 | $1.4 \times 10^{10}$ | Farhataziz & Ross (1977) |
| $(CH_3)_3CCO_2^- + OH \rightarrow$ | 9 | $1.4 \times 10^9$ | FR (1977) |
| $CH_3CH_2CH_2OH + OH \rightarrow$ | 2-2.2 | $3.2 \times 10^9$ | FR (1977) |
|  | 5-5.5 | $3.0 \times 10^9$ | FR (1977) |
|  | 5.6 | $2.7 \times 10^9$ | FR (1977) |
|  | 6 | $2.0 \times 10^9$ | FR (1977) |
| $CH_3CH_2CO_2H + OH \rightarrow$ | 1 | $2.0 \times 10^8$ | FR (1977) |
|  | 2-2.2 | $5.2 \times 10^8$ | FR (1977) |
| $CH_3CH_2CO_2^- + OH \rightarrow$ | 9 | $8.0 \times 10^8$ | FR (1977) |
| $C_3H_2CO_2CH_3$ | 6-7 | $1.4 \times 10^9$ | FR (1977) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING OH; BIMOLECULAR REACTIONS OF ORGANIC SPECIES
## TABLE K19

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $C_6H_5CH_3 + OH \rightarrow C_6H_5CH_2 + H_2O$ | 3 | $(3.0 \pm 0.7) \times 10^9$ | Farhataziz & Ross (1977) |
|  | 7 | $6.8 \times 10^9$ | FR (1977) |
| $o\text{-}\phi\text{-}(CH_3)_2 + OH \rightarrow$<br>(o-xylene) | 7 | $6.7 \times 10^9$ | FR (1977) |
| $m\text{-}\phi\text{-}(CH_3)_2 + OH \rightarrow$ | 7 | $7.5 \times 10^9$ | FR (1977) |
| $p\text{-}\phi\text{-}(CH_3)_2 + OH \rightarrow$ | 7 | $7.0 \times 10^9$ | FR (1977) |

KINETIC DATA: FREE RADICAL REACTIONS INVOLVING $HO_2$; BIMOLECULAR REACTIONS OF INORGANIC SPECIES
TABLE K20

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | 0-2 | $(1.35 \pm 0.3) \times 10^6$ | Farhataziz & Ross (1977) |
|  | 0.5-1.55 | $(2.4 \pm 0.4) \times 10^6$ | FR (1977) |
|  | 2 | $2.3 \times 10^6$ | FR (1977) |
|  | 1.7-3.0 | $2.1 \times 10^6$ | FR (1977) |
|  | 2.8-2.9 | $2.5 \times 10^6$ | FR (1977) |
|  | 5.6 | $(3.4 \pm 2.5) \times 10^6$ | FR (1977) |
|  | ——— | $8.6 \times 10^5$ | Bielski (1978) |
| $HO_2 + O_2^- \rightarrow HO_2^- + O_2$ | 0-5 | $3 \times 10^7$ | FR (1977) |
|  | 0-7.7 | $8.5 \times 10^7$ | FR (1977) |
|  | 2-9.7 | $7.9 \times 10^7$ | FR (1977) |
|  | 7 | $5.3 \times 10^7$ | FR (1977) |
| $Cu^{2+} + O_2^- \rightarrow Cu^+ + O_2$ | 2.3 | $1.5 \times 10^7$ | FR (1977) |
| $Fe^{2+} + HO_2 \rightarrow Fe^{3+} \cdot HO_2^-$ | 0-2.1 | $(2.1 \pm 0.4) \times 10^6$ | FR (1977) |
| $Fe^{3+} \cdot HO_2^- + 2H_2O \rightarrow Fe(OH)_2^+ + H^+ + H_2O_2$ |  |  |  |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING $HO_2$; BIMOLECULAR REACTIONS OF INORGANIC SPECIES

## TABLE K21

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH$ | 5.6 | 3.7 | Farhataziz & Ross (1977) |
| $HCO_3^- + O_2^- \rightarrow CO_3^- + HO_2^-$ | 5.5 | $1.5 \times 10^6$ | FR (1977) |
| $CO_3^- + O_2^- \rightarrow O_2 + CO_3^{2-}$ | 13 | $1.5 \times 10^9$ | FR (1977) |
| $Cu^+ + O_2^- \rightarrow Cu^+ + O_2$ | 3-6.5 | $8 \times 10^9$ | FR (1977) |
| $H_2O_2 + O_2^- \rightarrow OH + OH^- + O_2$ | 7 | 16 | FR (1977) |
| $HCO_3^- + O_2^- \rightarrow CO_3^{2-} + O_2$ |  | $4 \times 10^8$ | Behar et al. (1970) |
| $CO_3^- + H_2O_2 \rightarrow CO_3^{2-} + HO_2 + H^+$ |  | $8.0 \times 10^5$ | Behar et al. (1970) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING S(V); BIMOLECULAR REACTIONS OF $SO_3^-$, $SO_5^-$ and $SO_4^-$

TABLE K22

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $SO_3^- + p\text{-}CH_3O\text{-}\phi\text{-}OH \rightarrow$ | 9.2 | $4 \times 10^7$ | Huie & Neta (1984) |
| | 11.7 | $1.0 \times 10^8$ | HN (1984) |
| | 12.4 | $1.2 \times 10^8$ | HN (1984) |
| $\phi\text{-}OH + SO_3^- \rightarrow$ | 11.1 | $6 \times 10^5$ | HN (1984) |
| $SO_3^- + O_2 \rightarrow SO_5^-$ | 6.8 | $1.5 \times 10^9$ | HN (1984) |
| $SO_5^- + HSO_3^- \rightarrow SO_4^- + HSO_4^-$ | 6.8 | $3 \times 10^6$ | HN (1984) |
| $SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + H^+ + CO_3^-$ | | | Ross & Neta (1978) |
| $SO_5^- + p\text{-}CH_3O\text{-}\phi\text{-}OH \rightarrow$ | 6.7 | $5 \times 10^5$ | HN (1984) |
| | 9.2 | $5.5 \times 10^7$ | HN (1984) |
| | 11.7 | $1.3 \times 10^8$ | HN (1984) |
| $SO_3^- + O_2 \rightarrow$ | ? | $1.0 \times 10^8$ | Hayon et al. (1972) |
| $SO_3^{2-} + OH \rightarrow$ | ? | $5.5 \times 10^9$ | Farhataziz & Ross (1977) |
| $HSO_3^- + OH \rightarrow$ | ? | $9.5 \times 10^9$ | FR (1977) |
| $SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$ | ? | $2 \times 10^8$ | Ross & Neta (1978) |
| $SO_4^- + H_2O_2 \rightarrow HSO_4^- + HO_2$ | ? | $1.2 \times 10^7$ | Ross & Neta (1978) |

## KINETIC DATA: FREE RADICAL REACTIONS INVOLVING $CO_3^-$, $NO_3$ and $O^-$(pH $\geq$ 12)
## TABLE K23

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $CO_3^- + H_2O_2 \rightarrow CO_3^{2-} + H_2O_2^+$ |  | $8 \times 10^5$ | Behar et al. (1970) |
| $CO_3^- + CO_3^- \rightarrow CO_4^{2-} + CO_2$ |  | $6.2 \times 10^6$ | Weeks & Raboni (1966) |
| $CO_3^- + SO_3^- \rightarrow CO_2 + SO_4^{2-}$ |  | $5.5 \times 10^8$ | Lilie et al. (1978) |
| $CO_3^- + NO_2^- \rightarrow NO_2 + CO_3^{2-}$ |  | $4.0 \times 10^5$ | Ibid. |
| $Cl^- + NO_3 \rightarrow Cl + NO_3^-$ |  | $1.0 \times 10^8$ | Ross & Neta (1978) |
| $O^- + H_2O_2 \rightarrow H_2O + O_2^-$ | 11 | $8.0 \times 10^9$ | Rosinger & Dixon (1977) |
| $O^- + O^- + H_2O \rightarrow HO_2^- + OH^-$ |  | $1.0 \times 10^9$ | RD (1977) |
| $O^- + O_3 + H_2O \rightarrow O_2 + HO_2^- + OH^-$ |  | $8.0 \times 10^8$ | RD (1977) |
| $O^- + O_2 \rightarrow O_3^-$ | 13 | $2.5 \times 10^9$ | Farhataziz & Ross (1977) |
| $O^- + H_2O \rightarrow OH^- + OH$ | 8-8.8 | $(1.75 \pm 0.4) \times 10^6$ | FR (1977) |
| $O^- + O_3^- \rightarrow O_2 + O_2^{2-}$ | 13-13.7 | $(8 \pm 2) \times 10^8$ | FR (1977) |
| $O^- + SO_3^{2-} \rightarrow SO_3^- + 2OH^-$ | 14 | $3 \times 10^8$ | FR (1977) |
| $O^- + NO_2^- + H_2O \rightarrow 2OH^- + NO_2$ | 12 | $3.6 \times 10^8$ | FR (1977) |

KINETIC DATA: FREE RADICAL REACTIONS - TABLE K24

| Reaction | pH | $k(M^{-1}s^{-1})$ | Reference |
|---|---|---|---|
| $O_3 + OH \rightarrow HO_2 + O_2$ | — | $3.0 \times 10^9$ | Bahnemann & Hart (1982) |
| $O_3 + HO_2^- \rightarrow OH + O_2^- + O_2$ | 4-10 | $2.8 \times 10^6$ | Staehelin & Hoigne (1982) |
| $H_2 + OH \rightarrow H + H_2O$ | 3.0 | $3.5 \times 10^7$ | Farhataziz & Ross (1977) |
| $H + O_2 \rightarrow HO_2$ | 1.9 | $2.5 \times 10^{10}$ | FR (1977) |
| $O + O_2 \rightarrow O_3$ | | $3.0 \times 10^9$ | Amiachai & Treinin (1969) |
| $H + HO_2 \rightarrow H_2O_2$ | 0.4 | $2.0 \times 10^{10}$ | Anbar et al. (1975) |
| $ClO^- + H_2O_2 \rightarrow Cl^- + O_2 + H_2O$ | | $9.0 \times 10^9$ | Buxton & Subhani (1972) |
| $Cl + H_2O_2 \rightarrow HCl + HO_2$ (estimated) | | $4.5 \times 10^7$ | Graedel & Goldberg (1983) |
| $Cl + HO_2 \rightarrow HCl + O_2$ (estimated) | | $3.1 \times 10^9$ | Graedel & Goldberg (1983) |

## KINETIC DATA: FREE RADICAL SOURCES - TABLE K25

| Reaction | pH | k | Reference |
|---|---|---|---|
| $H_2O_2 + h\nu \rightarrow 2OH$ | | $2.5 \times 10^{-6} s^{-1*}$ | Chameides & Davis (1982) |
| $H_2O_2 + h\nu \xrightarrow{\lambda<390nm} 2OH$ | | $5.4 \times 10^{-7} s^{-1\dagger}$ | Graedel & Goldberg (1983) |
| $H_2O_2 + Fe^{2+} \rightarrow OH^- + OH + Fe^{3+}$ | 0-7 | $76\ M^{-1}s^{-1}$ | Walling (1975) |
| $O_3 + OH^- \rightarrow HO_2 + O_2^-$ | | $8 \times 10^{4} M^{-1.5} s^{-1}$ | Haruta & Takeyame (1981) |
| $O_3 + OH^- \rightarrow O_2^- + HO_2$ | | $7.0 \times 10^{1} M^{-1} s^{-1}$ | Staehelin & Hoigne (1982) |
| $O_3 + HO_2^- \rightarrow OH + O_2^- + O_2$ | 4-10 | $(2.8 \pm 0.5) \times 10^{6} M^{-1} s^{-1}$ | SH (1982) |
| $O_3 + H_2O \xrightarrow[\lambda<320nm]{h\nu} O_2 + H_2O_2$ | | $1.2 \times 10^{-5} s^{-1}$ | GG (1983) |
| $O_3 + H_2O \xrightarrow{h\nu} O_2 + H_2O_2$ | | $2 \times 10^{-5} s^{-1}$ | CD (1982) |

*Photolysis reactions are given for an altitude of 1.5 km, zenith angle of 30 and a cloud transmissivity of 0.5.

†Photolysis reactions are given for noon on May 1 at 41°N at an altitude of 1.5 km.

## KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) BY OZONE

### TABLE K26

| Rate ($\nu = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $\nu = k_1[HSO_3^-][O_3] + k_2[SO_3^{2-}][O_3]$ | $k_1 = 3.1 \times 10^5 M^{-1} s^{-1}$ | | |
| | $E_{a,1} = 46$ kJ mol$^{-1}$ | pH 0-4 | Erickson et al. (1977) |
| | $k_2 = 2.2 \times 10^9 M^{-1} s^{-1}$ | T = 25°C | |
| | $E_{a,2} = 43.9$ kJ mol$^{-1}$ | | |
| $\nu = (k_o[H_2O \cdot SO_2] + k_1[HSO_3^-]$ <br> $+ k_2 [SO_3^{2-}])[O_3]$ | $k_o = (2 \pm 2) \times 10^4 M^{-1} s^{-1}$ | | |
| | $k_1 = (3.2 \pm 0.2) \times 10^5 M^{-1} s^{-1}$ | pH 1-6 | Hoigne et al. (1984) |
| | $k_2 = (1.0 \pm 0.2) \times 10^9 M^{-1} s^{-1}$ | T = 22°C | |
| $\nu = (k_1 + k_2 [H^+]^{-1})[S(IV)][O_3]$ | $k_1 = 4.39 \times 10^{11} e^{-4131/T} (\pm 3 \times 10^4) M^{-1} s^{-1}$ | pH 3-6.2 | Maahs (1983) |
| | $k_2 = 2.56 \times 10^3 e^{-966/T} (\pm 15)\ s^{-1}$ | T = 10-25°C | |
| | $\log k = \log k_o + (\sqrt{\mu}/(1 + \sqrt{\mu})) - 0.3\mu$ | $\mu = 0.001$-$0.4M$ | |

TABLE K26 (continued)

| Rate ($\nu = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $\nu = k\,[O_3][S(IV)][H^+]^{-0.5}$ | $k = 1.9 \times 10^4 M^{-0.5} s^{-1}$ | pH 0-3<br>T = 25°C | Martin (1984) |
| $\nu = k\,[O_3][HSO_3^-][H^+]^{-0.5}$ | $k = (1.45 \pm 0.7) \times 10^4 M^{-0.5} s^{-1}$ | pH 1-5<br>T = 25°C | Penkett et al. (1979) |
| $\nu = kP_{O_3}H_{O_3}[HSO_3^-][H^+]^{-0.1}$ | $k = 4.4 \times 10^4 M^{-0.9} s^{-1}$ | pH 4-7<br>T = 25°C | Larson et al. (1978) |
| $\nu = k[Fe^{3+}][S(IV)][O_3][H^+]^n$ | $k_{obs} = 6.8 \times 10^5 M^{-1} min^{-1} ppm^{-1}$ | pH 4-6<br>T = 22°C<br>$[Fe^{3+}] \geq 10 \mu M$ | Harrison et al. (1982) |

## KINETIC DATA: INTRINSIC RATE LAW FOR THE OXIDATION OF S(IV) BY OZONE: TABLE K26 (cont.)

Based on data from Erickson et al. (1977), Hoigne et al. (1984), Maahs (1983), Martin (1984), and Penkett et al. (1979).

$$\nu = -d[S(IV)]/dt = (k_o\alpha_o + k_1\alpha_1 + k_2\alpha_2)\,[S(IV)][O_3]$$

$$\alpha_o = [H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad [SO_2 \cdot H_2O] = \alpha_o[S(IV)]$$

$$\alpha_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad [HSO_3^-] = \alpha_1[S(IV)]$$

$$\alpha_2 = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad [SO_3^{2-}] = \alpha_2[S(IV)]$$

$$\alpha_o + \alpha_1 + \alpha_2 = 1 \qquad [S(IV)] = [H_2O \cdot SO_2] + [HSO_3^-] + [SO_2^{2-}]$$

|  | Erickson | Hoigne | Maahs | Penkett | Martin |
|---|---|---|---|---|---|
| $k_o(M^{-1}s^{-1})$ | ~ $5.9 \times 10^2$ | $(2.0 \pm 2.0) \times 10^4$ | ——— | $1.6 \times 10^4$ | $3.7 \times 10^4$ |
| $k_1(M^{-1}s^{-1})$ | $3.1 \times 10^5$ | $(3.2 \pm 0.2) \times 10^5$ | $3.9 \times 10^5$ | $4.5 \times 10^5$ | $1.2 \times 10^6$ |
| $k_2(M^{-1}s^{-1})$ | $2.2 \times 10^9$ | $(1.0 \pm 0.2) \times 10^9$ | $1.2 \times 10^9$ | ——— | ——— |
| $E_{a,1}(kJ\ mol^{-1})$ | 46.0 | ——— | 33.9 | 30.0 | ——— |
| $E_{a,2}(kJ\ mol^{-1})$ | 43.9 | ——— | 30.7 | ——— | ——— |

## KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) BY HYDROGEN PEROXIDE

## TABLE K27

| Rate Law ($\nu = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $\nu = (k_o + k_p [H^+][H_2PO_4^-] + 9.5 \times 10^{12} 10^{-1.8pH} +$<br>$9.0 \times 10^{14} [SO_3^{2-}]) [H_2O_2][SO_3^{2-}]$ | $k_o = 0.2M^{-1}s^{-1}$<br>$k_p = 1.7 \times 10^{10} M^{-3}s^{-1}$<br>$E_a(K_o) = 63.5$ kJ-mol$^{-1}$ | T = 25°C<br>$\mu = 1.0M$<br>pH 7.9-12.8 | Mader (1958) |
| $\nu = (k[H^+] + k'[H_2PO_4^-]) [H_2O_2][S(IV)]\alpha_1$<br>$\alpha_1 \approx [H^+]/([H^+] + K_{a_2})$ | $k = 3.5 \times 10^8 M^{-2}s^{-1}$<br>$k' = 4.5 \times 10^3 M^{-2}s^{-1}$<br>(pH 6.4) | T = 12°C<br>$\mu = 1.0M$<br>pH 4-8 | Hoffmann & Edwards (1975) |
| $\nu = (k[H^+]^{0.7} + k_a[CH_3CO_2H])([H_2O_2][HSO_3^-])$<br>$k_1 = k[H_2O_2][H^+]^{0.7} + k_a [H_2O_2][HA]$ | $k = 2.46 \times 10^6 M^{-1}s^{-1}$<br>(pH 4.6)<br>$k_a = 1.9 \times 10^4 M^{-2}s^{-1}$<br>$\Delta H^\ddagger(k_1) = 24.9$ kJ-mol.$^{-1}$ | T = 20°C<br>$\mu = 0.2M$<br>pH 4-8 | Penkett et al. (1979) |
| $\nu = k[H_2O_2][HSO_3^-][H^+]/(k + [H^+])$ | $k = 5.6 \times 10^6 M^{-1}s^{-1}$<br>$k = 0.1M$ | T = 25°C<br>pH 0-3<br>$\mu$ (variable) | Martin & Damschen (1981) |

## KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) BY HYDROGEN PEROXIDE

### TABLE K27 (cont.)

| Rate Law ($\nu = -d[S(IV)]/dt$) | Rate Constants | Conditions | Reference |
|---|---|---|---|
| $\nu = k[H^+][H_2O_2][HSO_3^-]$ | $k = (8.0 \pm 0.18) \times 10^7 M^{-2} s^{-1}$ | pH 4.0 to 5.8<br>$\mu = < .01$<br>T = 22°C | Kunen et al. (1983) |
| $\nu = (k_2[H^+] + k_3[HA]k_1 k_{a_1}[H_2O_2][S(IV)]/ \{k_{-1} + k_2[H^+] + k_3[HA] (K_{a_1} + [H^+])\}$ | $k_1 = (2.6 \pm 0.5) \times 10^6 M^{-1} s^{-1}$<br>$\frac{k_2}{k_{-1}} = 16 \pm 4M^{-1}$<br>$\frac{k_2}{k_3} = (5 \pm 1) \times 10^2$ for HA = $CH_3CO_2H$<br>$\Delta H_1^{\ddagger} = 37 \pm 2kJ\text{-}mol^{-1}$<br>$\Delta S_1^{\ddagger} = 4 \pm 4\ Jk^{-1}mol^{-1}$ | T = 15°C<br>$\mu = 1.0M$<br>pH 0-3.4 | McArdle and Hoffmann (1983) |
| $\nu = k[H^+][H_2O_2][S(IV)]\alpha_1/(1 + 16[H^+])$ | $k = 4.16 \times 10^7 M^{-2} s^{-1}$ | no HA<br>pH 0-3 | McArdle and Hoffmann (1983) |

### KINETIC DATA: INTRINSIC RATE LAW FOR THE OXIDATION OF S(IV) BY $H_2O_2$

### TABLE K27 (cont.)

closed-phase pH 0-8

$$\nu = -\frac{d[S(IV)]}{dt} = k[H^+][H_2O_2][S(IV)]\alpha_1(1 + K[H^+])$$

$$\alpha_1 = K_{a_1}[H^+]/([H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2})$$

closed-phase pH $\geq$ 3

$$\nu = k[H^+][H_2O_2][S(IV)]\alpha_1$$

open-phase pH 0-8

$$\nu = kK_{a_1}P_{H_2O_2}K_{H,H_2O_2}P_{SO_2}K_{H,SO_2}/(1 + K[H^+])$$

$$[S(IV)] = P_{SO_2}K_{H,SO_2}\alpha_o^{-1} \quad [H_2O_2] = P_{H_2O_2}K_{H,H_2O_2}$$

| | Mader | Hoffmann | Penkett | Martin | Kunen | McArdle |
|---|---|---|---|---|---|---|
| $k(M^{-2}s^{-1})$ | $6.71 \times 10^9$ | $3.5 \times 10^8$ | $5.71 \times 10^7$ | $5.6 \times 10^7$ | $8.03 \times 10^7$ | $4.16 \times 10^7$ |
| $K (M^{-1})$ | — | — | — | 10 | — | 16 |
| $kK_{a_1}$ | $2.86 \times 10^8$ | $1.49 \times 10^7$ | $9.70 \times 10^5$ | $6.89 \times 10^5$ | $9.89 \times 10^5$ | $1.77 \times 10^6$ |
| $E_a(k)(kJmol^{-1})$ | — | — | 30.4 | — | — | 39.5 |
| T(°C) | 25 | 12 | 20 | 25 | 22 | 15 |
| k(25°C) | $6.71 \times 10^9$ | $7.26 \times 10^8$ | $7.50 \times 10^7$ | $5.60 \times 10^7$ | $9.44 \times 10^7$ | $7.25 \times 10^7$ |

Recommended values: $k = (7.45 \pm 1.57) \times 10^7 M^{-1}s^{-1}$ at 25°C, $K = 13M^{-1}$, $E_a = 39.5$ $kJmol^{-1}$

## KINETIC DATA: EMPIRICAL RATE LAWS FOR Fe(III)/Fe(II) CATALYZED AUTOXIDATION OF S(IV) IN AQUEOUS SOLUTION
## TABLE K28

| Rate ($\nu$ = -d[S(IV)]/dt) | Rate Constant | Conditions | Reference |
|---|---|---|---|
| $\nu = k[Fe(III)][S(IV)][H^+]^{-1}$ | $k = 0.82 s^{-1}$<br>(stopped-flow)<br>$k = 0.66 s^{-1}$<br>(potentiometric) | T = 25°C<br>pH 0-3<br>[S(IV)] > 100μM<br>(stopped-flow) | Martin (1984) |
| $\nu = k[Fe(III)][S(IV)][H^+]^{-1}$ | $k = 0.1 s^{-1}$ | pH 4-5<br>T = 20°C<br>[Fe(III)]~/μM<br>[S(IV)]~/mM<br>(pH stat) | Brimblecombe & Spedding (1974a) |
| $\nu = k[Fe(III)][S(IV)][H^+]^{-1}$ | $k = 7.6 \times 10^{-2} s^{-1}$ | T = 20°C<br>pH $\leq$ 4<br>($SO_2$ electrode) | Fuzzi (1978) |
| $\nu = k[Fe(III)][S(IV)]^2$ | $k = (9.7 \pm 2.7) \times 10^4 M^{-2} s^{-1}$ | pH $\geq$ 6<br>T = 20°C | Fuzzi (1978) |
| $\nu = k[Fe(III)][S(IV)]^2[H^+]^{-1}$ | $k = 40\ M^{-1} s^{-1}$ | pH 1.5-3<br>T = 10°C<br>[Fe(III)] > 100μM<br>[S(IV)] > 100μM | Neytzell-deWilde and Taverner (1958) |
| $\nu = \frac{k_1 [Fe(III)]^2[SO_3^{2-}]^2}{k_o[Fe(III)][SO_3^{2-}]_o + k_2[SO_4^{2-}]} + k_3[Fe(III)][SO_3^{2-}]$<br>($\nu \simeq k_3 [Fe(III)][S(IV)]\alpha_2$) | $k_o = 1 M^{-1} s^{-1}$<br>$k_1 = 3.6 \times 10^6 M^{-3} s^{-1}$<br>$k_2 = 2.5 \times 10^{-7} s^{-1}$<br>$k_3 = 4.5 \times 10^5 M^{-1} s^{-1}$ | T = 10°C<br>$\mu$ = 1.2M<br>pH 1.3-3.3<br>[Fe(III)] < 1mM<br>[S(IV)] < 1mM | Aubuchon (1976) |

## KINETIC DATA: EMPIRICAL RATE LAWS FOR Fe(III)/Fe(II) CATALYZED AUTOXIDATION OF S(IV) IN AQUEOUS SOLUTION

## TABLE K28 (cont.)

| Rate ($\nu = -d[S(IV)]/dt$) | Rate Constant | Conditions | Reference |
|---|---|---|---|
| $\nu = k[Fe(III)][S(IV)]^2$ | $k = 1.0 \times 10^7 M^{-2} s^{-1}$ | T = 20°C<br>pH $\geq$ 5 | Brimblecombe & Spedding (1974b) |
| $\nu = k[Fe(III)][HSO_3^-]^2[H^+]^{-1}$ | $k = 2.60 \times 10^2 M^{-1} s^{-1}$ | T = 20°C<br>optimized rate expression | Freiberg (1975) |
| $\nu = k[Fe(II)]_o^{1.16}[HSO_3^-]^{0.60}[H^+]^{-1}$<br>$k = \exp_{10}(2.32 - 1.26\mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}}))$ | $k = 2.09 \times 10^2$ | $\mu = o$<br>T = 25°C | Huss et al. (1982) |
| $\nu = k[Fe(II)]_o[HSO_3^-]^{0.61}/[H^+]^{1.1}[SO_4^{2-}]^{0.43}$<br>$k = \exp_{10}(0.79 - 0.99\mu 1/2/(1 + \mu^{\frac{1}{2}}))$ | $k = 6.2$ | $\mu = 0$<br>T = 25°C | Huss et al. (1982) |
| $\frac{-d[Fe(II)]}{dt} = \frac{d[Fe(III)]}{dt} = k_1\beta_2[Fe(II)][Fe(III)][SO_3^{2-}]$<br>$-k_2[Fe(III)][SO_3^{2-}]1/2$ | $k_1 = 1.15 \times 10^8 M^{-1} s^{-1}$<br>$k_2 = 7.34 \times 10^3 M^{-0.5} s^{-1}$<br>$\beta_2 = 1.58 \times 10^7 M^{-1}$ | T = 25°C | Kao (1979) |

## KINETIC DATA: INTRINSIC RATE LAW FOR THE OXIDATION OF S(IV) BY $O_2$ AS CATALYZED BY Fe(III)
### TABLE K28 (cont.)

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closed-phase pH 0-5

$$\nu = \frac{-d[S(IV)]}{dt} = k[Fe(III)][S(IV)]\alpha_2$$

$$\alpha_2 = K_{a_1}K_{a_2}/([H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2})$$

$$\text{at pH 4} \quad \alpha_2 \sim K_{a_2}/[H^+]$$

pH 3-5

$$\therefore \nu \simeq kK_{a_2}[Fe(III)][S(IV)][H^+]^{-1}$$

$$K_{a_2} = 6.31 \times 10^{-8} \qquad \mu = 0$$

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| | Aubuchon(1976) | Martin(1984) | Fuzzi(1978) | Brimblecombe | Neytzell-deWilde |
|---|---|---|---|---|---|
| $k(M^{-1}s^{-1})$ | $4.5 \times 10^5$ | $1.0 \times 10^7$ | $1.2 \times 10^6$ | $1.6 \times 10^6$ | $4.4 \times 10^5$ |
| T(°C) | 10 | 25 | 20 | 20 | 10 |
| $\mu$ | 1.2 | ~0 | ~0 | ~0 | ~0 |
| $k(20°C)^+$ | $9.3 \times 10^5$ | $7.4 \times 10^6$ | $1.2 \times 10^6$ | $1.6 \times 10^6$ | $9.1 \times 10^5$ |

recommended value*: $k = (1.2 \pm .32) \times 10^6 M^{-1}s^{-1}$

t assumes $\Delta H^{\ddagger}$ of 50 kJ $mol^{-1}$

*Martin value has been deleted from determination of average value.

## KINETIC DATA: EMPIRICAL RATE LAWS FOR $Mn^{2+}$-CATALYZED AUTOXIDATION OF S(IV) IN AQUEOUS SOLUTION

### TABLE K29

| Rate ($\nu = -d[S(IV)]/dt$) | Rate Constant | Conditions | Reference |
|---|---|---|---|
| $\nu = k[Mn^{2+}][S(IV)][H^+]^{-1}$ | $k = 2.5\ s^{-1}$ | pH 0 - 2<br>$[S(IV)] < 10^{-4}$ M<br>T = 25°C | Martin (1984) |
| $\nu = k[Mn^{2+}][S(IV)]$<br>$\nu = k[Mn^{2+}][HSO_3^-]$ | $k = (5.1 \pm 0.5) \times 10^3\ M^{-1}s^{-1}$<br>$E_a = 74.4$ kJ $mol^{-1}$ | T = 23.7°C<br>pH 2.5 - 8<br>$[Mn(II)] \sim 1\text{-}4\ \mu M$<br>$[S(IV)] \sim 1\text{-}10\ \mu M$ | Ibusuki & Barnes (1984) |
| $\nu = k[Mn^{2+}]^2[H^+]^{-1}$ | $k = 4.7\ s^{-1}$ | pH 0 - 2<br>$10^{-3}$ M > [S(IV)] $10^{-4}$ M | Martin (1984) |
| $\nu = k[Mn^{2+}][H^+]^{-1}$ | $k = 1.3 \times 10^{-5}\ Ms^{-1}$ | T = 10°C<br>pH 1.4 - 2.0<br>$[S(IV)] \cong 6 \times 10^{-4}$ M | Neytzell-deWilde & Taverner (1958) |
| $\nu = k[Mn^{2+}]^{1.7-2}$ | $k = 4.8 \times 10^2\ M^{-1}s^{-1}$ (25°C)<br>$k = 5\text{-}8 \times 10^2$ (35°C)<br>$E_a = 114$ kJ $mol^{-1}$ | T = 35°C<br>pH 2.4 - 3.3 | Hoather & Goodeve (1934) |

## KINETIC DATA: EMPIRICAL RATE LAWS FOR $Mn^{2+}$-CATALYZED AUTOXIDATION OF S(IV) IN AQUEOUS SOLUTION

## TABLE K29 (cont.)

| Rate ($\nu = -d[S(IV)]/dt$) | Rate Constant | Conditions | Reference |
|---|---|---|---|
| $\nu = k[Mn^{2+}]^2$ | $k = 3.6 \times 10^2\ M^{-1}s^{-1}$ | T = 25°C<br>pH 3 - 4<br>$[Mn(II)] > 100\ \mu M$ | Coughanowr & Krause (1965) |
| $\nu = k_1[Mn(II)]_0^2 + k_2[Mn(II)]_0[HSO_3^-]$<br>$k_1 = \exp_{10}(6.39-4.07\ \mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})$<br>$k_2 = \exp_{10}(3.48-1.01\ \mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})$ | $k_1 = 2.45 \times 10^6\ M^{-1}s^{-1}$<br>$k_2 = 3.02 \times 10^3\ M^{-1}s^{-1}$ | $\mu = 0$<br>T = 25.0°C<br>$[Mn(II)] = 10^{-4}$-$10^{-5}$ M | Huss et al. (1982) |

### KINETIC DATA: INTRINSIC RATE LAW FOR $Mn^{2+}$ CATALYSIS OF S(IV) AUTOXIDATION

### TABLE K29 (cont.)

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conditions

$[S(IV)] \leq 100\ \mu M$ — $\nu_2 = k_2[Mn(II)][S(IV)]\alpha_1$

$[Mn(II)] \leq 10\ \mu M$ — $\alpha_1 = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$

at pH 1 $\nu \cong k_2K_{a1}[Mn^{2+}][S(IV)][H^+]^{-1}$

conditions

$[S(IV)] > 100\ \mu M$

$[Mn(II)] > 10\ \mu M$

$\nu_1 = k_1\beta_1[Mn^{2+}]^2[H^+]^{-1}$ $\beta_1 = [Mn_2OH^{3+}][H^+]/[Mn^{2+}][H_2O]$

$\log \beta_1 = -9.9$

---

| | Martin | Ibusuki | Hoather | Coughanowr | Huss | Taverner |
|---|---|---|---|---|---|---|
| $k_1 (M^{-1}s^{-1})$ | $3.7 \times 10^{10}$ | -- | $1.9 \times 10^9$ | $2.85 \times 10^9$ | -- | $5.16 \times 10^8$ |
| $k_2 (M^{-1}s^{-1})$ | $2.03 \times 10^3$ | $5.1 \times 10^3$ | -- | -- | $3.02 \times 10^3$ | -- |
| $E_{a,1}$ (kJ-mol$^{-1}$) | | -- | 114 | -- | -- | -- |
| $E_{a,2}$ (kJ-mol$^{-1}$) | | 74.4 | -- | -- | -- | -- |
| T(°C) | 25 | 23.7 | 35 | 25 | 25 | 10 |

Recommended values: $k_2 = (3.4 \pm 1.6) \times 10^3\ M^{-1}s^{-1}$ $k_1 = (2.0 \pm 0.5) \times 10^9\ M^{-1}s^{-1}$

$E_{a,2} = 74.4\ kJ\ mol^{-1}$

## KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) TO S(VI)
## TABLE K30

| Reaction | Rate Law | Constant & Conditions | Reference |
|---|---|---|---|
| $CH_3OOH + HSO_3^- \rightarrow H^+ + SO_4^{2-} + CH_3OH$<br>(methyl hydroperoxide) | $\nu = k_3[H^+][CH_3O_2H][HSO_3^-]$ | $k_3 = (1.75 \pm 0.3) X 10^7 M^{-2} s^{-1}$<br>$E_a(k_3) = 31.61$ kJ-mol$^{-1}$<br>pH 3-6; T=18°C | Lind et al. (1984) |
| $CH_3\overset{\overset{O}{\Vert}}{C}OOH + HSO_3^- \rightarrow H^+ + SO_4^{2-} + CH_3CO_2H$<br>(peroxyacetic acid) | $\nu = (k_3[H^+] + k_2)[HSO_3^-][CH_3\overset{\overset{O}{\Vert}}{C}O_2H]$ | $k_3 = (3.64 \pm 0.41) X 10^7 M^{-2} s^{-1}$<br>$E_a(k_3) = 33.21$ kJ-mol$^{-1}$<br>$k_2 = 6.01 X 10^2 M^{-1} s^{-1}$<br>pH 3-6; T=18°C<br>$\mu \sim 0$ | Ibid. |
| $CH_3\overset{\overset{O}{\Vert}}{C}OONO_2 + HSO_3^- \rightarrow$<br>(peroxyacetylnitrate) | $\nu = k[PAN][HSO_3^-]$ | $k(pH\ 5.6) = 3 X 10^3 M^{-1} s^{-1}$<br>$k(pH\ 4.9) = 5 X 10^2 M^{-1} s^{-1}$ | Lee (1984) |
| $H^+ + SO_4^{2-} + CH_3CO_2^- + NO_2^+$ | $\nu = k' k_{a_2}[PAN][HSO_3^-][H^+]^{-1}$ | $k' = 1.1 X 10^5 M^{-1} s^{-1}$ | |
| $2HNO_2 + 2SO_2 \cdot H_2O \rightarrow 2SO_4^{2-}$<br>$+ N_2O + H_2O + 4H^+$ | $\nu = k[HNO_2]_T[S(IV)][H^+]^{1/2}$ | $k = 1.42 X 10^2 [H^+]^{1/2} M^{-1} s^{-1}$<br>pH < 3 | Martin et al. (1984) |
| $NO_2^- + 2HSO_3^- \rightarrow HON(SO_3)_2^{2-} + OH^-$ | $\nu = [H^+][NO_2^-][HSO_3^-]$ | $k = 4.8 X 10^3 M^{-2} s^{-1}$<br>$E_a = 25.5$ kJ mol$^{-1}$<br>pH 5-7 | Oblath et al. (1984) |
| $HSO_3^- + 1/2\ O_2 \xrightarrow{soot} HSO_4^-$ | $\nu = k_1[C_x][O_2]^{0.69}[S(IV)]^2/$<br>$(1 + k_1[S(IV)] + k_2[S(IV)]^2)$ | $k_1 = 2.54 X 10^7 M^{-2.31} L^{2.69} g^{-1} s^{-1}$<br>$k_1 = 3.06 X 10^6$<br>$k_2 = 1.5 X 10^{12}$ | Brodzinsky et al. (1980) |

KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) and N(III)
IN AQUEOUS SOLUTION
TABLE K31

| Reaction | Rate Law | Constant & Conditions | Reference |
|---|---|---|---|
| $HNO_2 + HSO_3^- \rightarrow ONSO_3^- + H_2O$<br>$ONSO_3^- + HSO_3^- \rightarrow HON(SO_3)_2^{2-} + H_2O$<br>$ONSO_3^- + H^+ \rightarrow HNO + HSO_4^- + H^+$<br>$2HNO \rightleftharpoons H_2N_2O_2 \rightarrow N_2O + H_2O$ | $\nu = k_1[H^+]^2[NO_2^-]$<br>$+k_2[H^+][HSO_3^-][NO_2^-]$<br>$+k_3[HSO_3^-]^2[NO_2^-]$ | $k_1 = 8 \times 10^5 M^{-2}s^{-1}$<br>$k_2 = 3.8 \times 10^3 M^{-2}s^{-1}$<br>$k_3 = 9.0 \times 10^{-4} M^{-2}s^{-1}$ | Oblath et al. (1982) |
| $HSO_3^- + 1/2\ O_2 \xrightarrow{\text{soot}} HSO_4^-$ | $\nu = \dfrac{k_1K_1[C_x][S(IV)]^2}{1+k_3[S(IV)]+K_2[S(IV)]^2}$ | $k_1 = 1.04 \times 10^{-7}$ mole $g^{-1}s^{-1}$<br>$K_1 = 4.92 \times 10^8\ M^{-2}$<br>$K_2 = 2.96 \times 10^5\ M^{-1}$ | Benner et al. (1981) |
| $HSO_3^- + 1/2\ O_2 \xrightarrow{Cu^{2+}} HSO_4^-$ | $\nu = (k_1 + k_2[Cu^{2+}])[SO_3^{2-}]$ | $k_1 = 1.3 \times 10^{-2}s^{-1}$<br>$k_3 = 2.5 \times 10^6 M^{-1}s^{-1}$<br>$pH_o = 8.7$<br>$Cu(OH)_s$<br>T = 25°C | Fuller & Christ (1941) |
| $HSO_3^- + 1/2\ O_2 \xrightarrow{Cu^{2+}} HSO_4^-$ | $\nu = 0.5k_1[Cu^{2+}]^{1/2}[SO_3^{2-}]^{3/2}$ | pH 7-9<br>$k_1 = 1.2 \times 10^3 M^{-1}s^{-1}$<br>$E_a = 76$ kJ-mol$^{-1}$<br>T = 25°C | Barron & O'Hern |
| $HSO_3^- + 1/2\ O_2 \xrightarrow{Co^{2+}} HSO_4^-$ | $\nu = \dfrac{k[Co^{2+}]_o[SO_3^{2-}][O_2]}{1 + k_2[SO_3^{2-}]}$ | $k_1 = 1.96 \times 10^9 M^{-2}s^{-1}$<br>$k_2 = 4.74 \times 10^2 s^{-1}$<br>T = 20°C<br>pH 8-8.3 | Srivastara et al.(1968) |

## KINETIC DATA: EMPIRICAL RATE LAWS FOR THE OXIDATION OF S(IV) AND N(III)/N(IV)

### TABLE K31 (cont.)

| Reaction | Rate Law | Constant & Conditions | Reference |
|---|---|---|---|
| $2\ HNO_2 + O_2 \rightarrow 2HNO_3$ | $\nu = k[HNO_2]^2[O_2]$ | $k = 3.6 \times 10^1 M^{-2} s^{-1}$<br>T = 25°C<br>pH 1-4 | Martin et al. (1981) |
| $HNO_2 + O_3 \rightarrow HNO_3 + O_2$ | $\nu = k[O_3][NO_2^-]$ | $k = 5.0 \times 10^5$<br>pH 1-4<br>T = 25°C | Ibid. |
| $HNO_2 + H_2O_2 \xrightarrow{H^+} HOONO + H_2O$ | $\nu = k[H^+][H_2O_2][HNO_2]$ | $k = 4.6 \times 10^3$<br>T = 25°C | Ibid. |
| $HOONO \xrightarrow{H^+} HNO_3$ |  | pH 0-4 |  |
| $2NO_2(aq) + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$ | $\nu = k[NO_2]^2$ | $k = 7.0 \times 10^7 M^{-1} s^{-1}$<br>T = 25°C | Schwartz (1984) |
| $NO(aq) + NO_2(aq) + H_2O \rightarrow 2H^+ + 2NO_2^-$ | $\nu = k[NO][NO_2]$ | $k = 3.0 \times 10^8 M^{-1} s^{-1}$ | Schwartz (1984) |
| $N_2O_4(aq) \xrightarrow{H_2O} 2H^+ + NO_2^- + NO_3^-$ | $\nu = k[N_2O_4]$ | $k = 1 \times 10^3 s^{-1}$ | Ibid. |
| $2NO_2(aq) = N_2O_4(aq)$ | $K = [N_2O_4]/[NO_2]^2$ | $K = 7 \times 10^4 M^{-1}$ | Ibid. |
| $N_2O_4\ (g) = N_2O_4(aq)$ | $K_H = [N_2O_4]/P_{N_2O_4}$ | $K_H = 1.0\ M\ atm^{-1}$ | Ibid. |
| $N_2O_3(aq) \xrightarrow{H_2O} 2H^+ + 2NO_2^-$ | $\nu = k[N_2O_3]$ | $k = 1.0 \times 10^3 M^{-1} s^{-1}$ | Ibid. |

# APPENDIX B: THERMODYNAMIC DATA

# FOR AQUEOUS-PHASE REACTIONS

## THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY

## TABLE T1

| Reaction | $\mu$‡ | $K_H$ | $pK_H$ * | $\Delta H^\circ_{298}$ † | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | 0 | 1.24 | -0.095 | - 26.13 | 25 | Smith & Martell (1976) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | 1.0 | 1.07 | -0.03 | —— | 25 | SM (1976) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | 3.0 | 1.15 | -0.06 | —— | 25 | SM (1976) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | | 1.67 | -0.223 | | 15 | Rabe & Harris (1963) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | 0 | 1.16[a] | -0.066 | - 41.38[a] | 25 | Guthrie (1979) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | | 1.20 | -0.079 | | 25 | RH (1963) |
| $SO_2(g) + H_2O \rightleftharpoons H_2O \cdot SO_2$ | | 1.24[b] | -0.094 | - 26.23 | 25 | Maahs (1982) |
| $H_2S(g) \rightleftharpoons H_2S(\ell)$ | | $1.02 \times 10^{-3}$ | 2.99 | - 18.80 | 25 | Loomis (1928) |
| $H_2SO_4(g) \rightleftharpoons 2H^+ + SO_4^{2-}$ | | $1.27 \times 10^{15}$ | -15.1 | -166.78 | 25 | L (1952)/JANAF (1970) |
| $(CH_3)_2S(g) \rightleftharpoons (CH_3)_2S(\ell)$ | | 0.62 | | | 25 | |

*$pK \equiv -\log k$ K is in M $atm^{-1}$ † $\Delta H^\circ_{298}$ in units of kJ $mol^{-1}$ ‡ ionic strength

a. Calculated from $\Delta H^\circ_f$ and $\Delta G^\circ_f$ values b. Critically determined value

Note: When more than one value for identical conditions has been cited the recommended values are underlined.

## THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY

### TABLE T2

| Reaction | μ | $K_H$ | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HNO_3(g) \rightleftharpoons H^+ + NO_3^-$ | | $3.23 \times 10^6$ | -6.51 | - 72.31 | 25 | Schwartz & White (1981) |
| $HNO_2(g) \rightleftharpoons HNO_2(\ell)$ | | 49 | -1.7 | - 39.71 | 25 | SW (1981) |
| $PAN(g) \rightleftharpoons PAN(\ell)$[a] | | 5 ± 1 | -0.7 | ____ | 10 | Holdren et al. (1984) |
| $PAN(g) \rightleftharpoons PAN(\ell)$ | | 3.6 ± 0.2 | -0.556 | -49.12 | 22 | Lee (1984) |
| $PAN(g) \rightleftharpoons PAN(\ell)$ | | 8.3 ± 0.5 | -0.919 | -49.12 | 10.2 | L (1984) |
| $NO(g) \rightleftharpoons NO(\ell)$ | | $1.9 \times 10^{-3}$ | 2.72 | -12.29 | 25 | Schwartz (1984) |
| $HNO_3(g) \rightleftharpoons HNO_3(aq)$ | | $2.1 \times 10^5$ | -5.32 | | 25 | S (1984) |
| $2NO_2(g) + H_2O \rightleftharpoons HNO_2(\ell)$ $+H^+ + NO_3^-$ | | $4.78 \times 10^5$ | -5.68 | -107.0 | 25 | Schwartz & White (1983) |
| $NO_2(g) \rightleftharpoons NO_2(\ell)$ | | $1.00 \times 10^{-2}$ | 2.00 | | 25 | S (1984) |
| $NO_2(g) \rightleftharpoons NO_2(\ell)$ | | $2.35 \times 10^{-2}$ | 1.63 | | 15°C | Komiyama & Inoue (1980) |
| $NO_2(g) \rightleftharpoons NO_2(\ell)$ | | $4.1 \times 10^{-2}$ | 1.39 | | 25°C | Andrew and Hanson (1961) |
| $NO_2(g) \rightleftharpoons NO_2(\ell)$ | | $7.0 \times 10^{-3}$ | 2.16 | | 22°C | Lee & Schwartz (1981) |

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a. PAN = peroxyacetyl nitrate

THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY

TABLE T2 (continued)

| Reaction | μ | $K_H$ | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $N_2O(g) \rightleftharpoons N_2O(\ell)$ | | $2.5 \times 10^{-2}$ | 1.60 | | 25 | S (1984) |
| $NH_3(g) + H_2O \rightleftharpoons NH_3 \cdot H_2O$ | | 58.9 | -1.77 | -34.15 | 25 | Sillen & Martell (1964) |
| $NH_3(g) + H_2O \rightleftharpoons NH_3 \cdot H_2O$ | | 62 | -1.79 | | 25 | S (1984) |
| $NH_3(g) \rightleftharpoons NH_3(\ell)$ | | 56.7 | -1.75 | -34.61 | 25 | Latimer (1952) |
| $NO_2(g) \rightleftharpoons NO_2(\ell)$ | | $8.57 \times 10^{-3}$ | 2.07 | | 25 | Latimer (1952 & LS (1981) |
| $HNO_3(g) \rightleftharpoons H^+ + NO_3^-$ | | $2.69 \times 10^{3}$ | -6.43 | -72.20 | 25 | L (1952)/JANAF (1970) |
| $NOCl(g) + H_2O \rightleftharpoons HNO_2(\ell) + H^+ + Cl^-$ | | $4.98 \times 10^{27}$ | -27.7 | | 25 | L (1952) |

THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY

TABLE T3

| Reaction | $\mu$ | $K_H$ | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $CO_2(g) + H_2O \rightleftharpoons H_2O \cdot CO_2$ | 0 | $3.4 \times 10^{-2}$ | 1.464 | -20.27 | 25 | SM (1976) |
| $CO_2(g) + H_2O \rightleftharpoons H_2O \cdot CO_2$ | 1.0 | $3.1 \times 10^{-2}$ | 1.51 |  | 25 | SM (1976) |
| $CO_2(g) + H_2O \rightleftharpoons H_2O \cdot CO_2$ | 3.0 | $2.8 \times 10^{-2}$ | 1.55 |  | 25 | SM (1976) |
| $CH_2O(g) + H_2O \rightleftharpoons CH_2O \cdot H_2O$ |  | $6.3 \times 10^{3}$ | -3.80 | -53.71 | 25 | Ledbury & Blair (1925) |
| $CH_2O(g) \rightleftharpoons CH_2O(\ell)$ |  | $3.46^{a}$ | -0.539 |  | 25 | This work |
| $HCl(g) \rightleftharpoons H^+ + Cl^-$ |  | $1.66 \times 10^{5}$ | -5.22 |  | 25 | Loomis (1928) |
| $HCl(g) \rightleftharpoons H^+ + Cl^-$ |  | $2.05 \times 10^{6}$ | -6.31 | -75.07 | 25 | Latimer (1952) |

a. Calculated from $[CH_2O]_T = K_H P_{CH_2O}(1 + K_a)$ $K_a = [CH_2(OH)_2]/[CH_2O] = 1.82 \times 10^3$

THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY, HYDROCARBONS

TABLE T4

| Reaction | μ (M) | $K_H$ (M $atm^{-1}$) | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $CH_4(g) \rightleftharpoons CH_4(\ell)$ | | $1.5 \times 10^{-3}$ | 2.82 | | 25 | Calvert (1984)* |
| $C_2H_6(g) \rightleftharpoons C_2H_6(\ell)$ | | $2.0 \times 10^{-3}$ | 2.70 | | 25 | Calvert (1984)* |
| $C_3H_8(g) \rightleftharpoons C_3H_8(\ell)$ | | $1.42 \times 10^{-3}$ | 2.85 | | 25 | Calvert (1984)* |
| $n\text{-}C_4H_{10}(g) \rightleftharpoons n\text{-}C_4H_{10}(\ell)$ | | $1.06 \times 10^{-3}$ | 2.97 | | 25 | Calvert (1984)* |
| $i\text{-}C_4H_{10}(g) \rightleftharpoons i\text{-}C_4H_{10}(\ell)$ | | $8.44 \times 10^{-4}$ | 3.07 | | 25 | Calvert (1984)* |
| $C_2H_4(g) \rightleftharpoons C_2H_4(\ell)$ | | $4.67 \times 10^{-3}$ | 2.33 | | 25 | Calvert (1984)* |
| $C_3H_6(g) \rightleftharpoons C_3H_6(\ell)$ | | $4.76 \times 10^{-3}$ | 2.32 | | 25 | Calvert (1984)* |
| $1\text{-}C_4H_8(g) \rightleftharpoons 1\text{-}C_4H_8(\ell)$ | | $1.56 \times 10^{-3}$ | 2.81 | | 25 | Calvert (1984)* |
| $i\text{-}C_4H_8(g) \rightleftharpoons i\text{-}C_4H_8(g)$ | | $1.35 \times 10^{-3}$ | 2.87 | | 25 | Calvert (1984)* |
| $C_6H_6(g) \rightleftharpoons C_6H_6(\ell)$ | | $1.84 \times 10^{-1}$ | 0.74 | | 25 | Calvert (1984)* |
| toluene(g) $\rightleftharpoons$ toluene($\ell$) | | $1.51 \times 10^{-1}$ | 0.82 | | 25 | Calvert (1984)* |
| o-xylene(g) $\rightleftharpoons$ o-xylene($\ell$) | | $2.03 \times 10^{-1}$ | 0.69 | | 25 | Calvert (1984)* |
| p-xylene(g) $\rightleftharpoons$ p-xylene($\ell$) | | $1.45 \times 10^{-1}$ | 0.84 | | 25 | Calvert (1984)* |
| naphthalene(g) $\rightleftharpoons$ naphthalene($\ell$) | | 2.36 | -0.37 | | 25 | Calvert (1984)* |
| anthracene(g) $\rightleftharpoons$ anthracene($\ell$) | | 16.9 | -1.23 | | 25 | Calvert (1984)* |
| 3,4-benzopyrene(g) $\rightleftharpoons$ 3,4-benzopyrene($\ell$) | | $7.2 \times 10^{5}$ | -5.86 | | 25 | Calvert (1984)* |

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*taken from a compilation provided by JGC

## THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY: CARBONYL COMPOUNDS

## TABLE T5

| Reaction | μ (M) | $K_H$ (M atm$^{-1}$) | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $CH_2O(g) + H_2O \rightleftharpoons CH_2(OH)_2$ | | $6.3 \times 10^3$ | +3.8 | -53.71 | 25 | Ledbury & Blair (1925) |
| $CH_3CHO(g) \rightleftharpoons CH_3CHO(\ell)$ | | 15 | +1.18 | | 25 | Calvert (1984) |
| $CH_2 = CH_2CHO(g) \rightleftharpoons CH_2 = CH_2\text{-}CHO(\ell)$ | | 8.2 | +0.91 | | 25 | Calvert (1984) |
| $CH_3\text{-}CH = CH\text{-}CHO(g) \rightleftharpoons CH_3\text{-}CH = CH\text{-}CHO(g)$ | | 51 | +1.71 | | 25 | Calvert (1984) |
| $CH_3COCH_3(g) \rightleftharpoons CH_3COCH_3(g)$ | | 30 | +1.48 | | 25 | Calvert (1984) |
| $\phi\text{-}CHO(g) \rightleftharpoons \phi\text{-}CHO(\ell)$ | | 36 | 1.56 | | 25 | Calvert (1984) |
| $(CHO)_2(g) \rightleftharpoons (CHO)_2(\ell)$ | | 190 | 2.28 | | 25 | Calvert (1984) |
| $HO\text{-}\phi\text{-}CHO(g) \rightleftharpoons HO\text{-}\phi\text{-}CHO(\ell)$ | | $4.0 \times 10^5$ | 5.60 | | 25 | Calvert (1984) |

## THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY; WEAK ACIDS AND ALCOHOLS

TABLE T6

| Reaction | $\mu$ (M) | $K_H$ (M atm$^{-1}$) | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HCO_2H(g) \rightleftharpoons HCO_2H(\ell)$ |  | 83 |  |  | 25 | Calvert (1984) |
| $HCO_2H(g) \rightleftharpoons HCO_2^- + H^+$ |  | 230 (pH 4) |  |  | 25 | Calvert (1984) |
| $HO_2CCO_2H(g) \rightleftharpoons HO_2CCO_2H$ |  | $7.2 \times 10^3$ |  |  | 25 | Calvert (1984) |
| $HO_2CCO_2H(g) \rightleftharpoons C_2O_4{}^{2-} + 2H^+$ |  | $7.0 \times 10^6$ (pH 4) |  |  | 25 | Calvert (1984) |
| $CH_3CO_2H(g) \rightleftharpoons CH_3CO_2H(\ell)$ |  | $8.6 \times 10^3$ |  |  | 25 | Calvert (1984) |
| $CH_3CO_2H(g) \rightleftharpoons CH_3CO_2^- + H^+$ |  | $1.0 \times 10^4$ (pH 4) |  |  | 25 | Calvert (1984) |
| $CH_3OH(g) \rightleftharpoons CH_3OH(\ell)$ |  | 220 |  |  | 25 | Calvert (1984) |
| $C_2H_5OH(g) \rightleftharpoons C_2H_5OH(\ell)$ |  | 200 |  |  | 25 | Calvert (1984) |
| $o\text{-}\phi\text{-}(OH)_2(g) \rightleftharpoons o\text{-}\phi\text{-}(OH)_2(\ell)$ |  | 830 |  |  | 25 | Calvert (1984) |
| $p\text{-}\phi\text{-}(OH)_2(g) \rightleftharpoons p\text{-}\phi\text{-}(OH)_2(\ell)$ |  | $1.3 \times 10^3$ |  |  | 25 | Calvert (1984) |

### THERMODYNAMIC DATA: HENRY'S LAW EQUILIBRIA RELEVANT TO DROPLET PHASE CHEMISTRY; OXIDANTS

### TABLE T7

| Reaction | μ | $K_H$ | $pK_H^*$ | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $H_2O_2(g) \rightleftharpoons H_2O_2(\ell)$ | | $7.08 \times 10^4$ | -4.85 | -60.6 | 25 | Martin & Damschen (1981) |
| $H_2O_2(g) \rightleftharpoons H_2O_2(\ell)$ | | $1.42 \times 10^5$ | -5.15 | | 20 | Yoshizumi et al. (1984) |
| $H_2O_2(g) \rightleftharpoons H_2O_2(\ell)$ | | $1.7 \times 10^5$ | -5.23 | | 13 | Okita (1984) |
| $H_2O_2(g) \rightleftharpoons H_2O_2(\ell)$ | | $4.03 \times 10^4$ | -4.60 | -54.97 | 25 | Latimer (1952)/JANAF (1971) |
| $O_3(g) \rightleftharpoons O_3(\ell)$ | | $9.33 \times 10^{-3}$ | 2.03 | -21.07 | 25 | Landolt-Börnstein (1976) |
| $O_3(g) \rightleftharpoons O_3(\ell)$ | | $9.4 \times 10^{-3}$ | 2.03 | -19.86 | 25 | Kirk-Othmer (1981) |
| $O_3(g) \rightleftharpoons O_3(\ell)$ | | $1.3 \times 10^{-2}$ | 1.89 | | 25 | Briner & Perrottet (1939) |
| $O_3(g) \rightleftharpoons O_3(\ell)$ | | $1.22 \times 10^{-2}$ | 1.91 | -18.75 | 25 | Loomis (1928) |
| $O_2(g) \rightleftharpoons O_2(\ell)$ | | $1.26 \times 10^{-3}$ | 2.90 | -14.96 | 25 | Perry (1963) |
| $O_2(g) \rightleftharpoons O_2(\ell)$ | | $1.22 \times 10^{-3}$ | 2.91 | -14.99 | 25.1 | Carpenter (1966) |
| $O_2(g) \rightleftharpoons O_2(\ell)$ | | $1.27 \times 10^{-3}$ | 2.90 | -14.14 | 25 | Loomis (1928) |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
## S(IV) ACID-BASE EQUILIBRIA
## TABLE T8

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.23 \times 10^{-2}$ | 1.91* | 16.72 | 25 | Smith & Martell (1976) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0.1 | $2.40 \times 10^{-2}$ | 1.62* | | 25 | Smith & Martell (1976) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 1.0 | $4.27 \times 10^{-2}$ | 1.37* | | 25 | Smith & Martell (1976) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 3.0 | $1.91 \times 10^{-2}$ | 1.72* | | 25 | Smith & Martell (1976) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.30 \times 10^{-2}$ | 1.89 | 16.72 | 25 | Johnson and Leppla (1934) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.36 \times 10^{-2}$ | 1.87 | | 25 | Yui (1940) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.39 \times 10^{-2}$ | 1.86 | | 25 | Ellis & Anderson (1961) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.43 \times 10^{-2}$ | 1.84 | 16.20 | 25 | Deveze & Rumpf (1964) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.38 \times 10^{-2}$ | 1.86 | | 25 | Huss & Eckert (1977) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.32 \times 10^{-2}$ | 1.88* | 16.20 | 25 | Maahs (1982) |
| $HO_2SOH \rightleftharpoons H^+ + HOSO_2^-$ | 0 | $5.01 \times 10^{-3}$ | 2.3 | | 25 | Guthrie (1979) |
| $HSO_2OH \rightleftharpoons H^+ + H\text{-}SO_3^-$ | 0 | $3.98 \times 10^{2}$ | -2.6 | | 25 | Guthrie (1979) |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | 0 | $1.30 \times 10^{-2}$ | 1.89 | | 25 | Kao (1979) |

*Critically compiled values.

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY:
## S(IV) ACID-BASE EQUILIBRIA
### TABLE T9

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $6.61 \times 10^{-8}$ | 7.18* | -12.5 | 25 | Smith & Martell (1976) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0.1 | $1.62 \times 10^{-7}$ | 6.79* | | 20 | Smith & Martell (1976) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 1.0 | $4.57 \times 10^{-7}$ | 6.34* | | 25 | Smith & Martell (1976) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 3.0 | $4.79 \times 10^{-7}$ | 6.32* | | 25 | Smith & Martell (1976) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $6.31 \times 10^{-8}$ | 7.20 | | 25 | Yui (1940) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $6.31 \times 10^{-8}$ | 7.20 | | 25 | Hayon et al. (1972) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $6.24 \times 10^{-8}$ | 7.20 | | 25 | Tartar & Garretson (1941) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $7.1 \times 10^{-8}$ | 7.15 | | 25 | Cuta (1957) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $6.42 \times 10^{-8}$ | 7.19* | -11.8 | 25 | Maahs (1982) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $1.23 \times 10^{-7}$ | 6.91 | | 25 | Rhee & Dasgupta (1984) |
| $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ | ~0.1 | $7.0 \times 10^{-2}$ | 1.15 | | 20 | Golding (1960) |
| $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ | 0 | $7.6 \times 10^{-2}$ | 1.12 | | 25 | Bourne et al. (1974) |
| $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ | 2.0 | $3.4 \times 10^{-1}$ | 0.47 | | 25 | Ibid. |
| $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ | 1.0 | $8.8 \times 10^{-2}$ | 1.06 | | 25 | Connick et al. (1982) |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | 0 | $1.29 \times 10^{-7}$ | 6.89 | -14.58 | 25 | Kao |

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*Critically compiled values.

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
## S(IV) EQUILIBRIA
## TABLE T10

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $2HSO_3^- \rightleftharpoons (HSO_3^-)_2$ | 0 | $1.75 \times 10^{3}$ | -3.24 | | 25 | Rhee & Dasgupta (1984) |
| $(HSO_3^-)_2 \rightleftharpoons (HSO_3 \cdot SO_3^{2-}) + H^+$ | 0 | $1.13 \times 10^{-8}$ | 7.95 | | 25 | Rhee & Dasgupta (1984) |
| $HSO_3^- + SO_3^{2-} \rightleftharpoons HSO_3 \cdot SO_3^{3-}$ | | $1.61 \times 10^{2}$ | -2.21 | | 25 | Ibid. |
| $HSO_3 \cdot SO_3^{3-} \rightleftharpoons H^+ + 2SO_3^{2-}$ | | $7.65 \times 10^{-10}$ | 9.12 | | 25 | Ibid. |
| $(HSO_3^-)_2 \rightleftharpoons S_2O_5^{2-} + H_2O$ | | $1.99 \times 10^{-5}$ | 4.70 | | 25 | Ibid. |
| $HO\text{-}SO_2^- \rightleftharpoons H\text{-}SO_3^-$ | | $3.98 \times 10^{1}$ | -1.60 | | 25 | Guthrie (1979) |
| $HO\text{-}SO_2^- \rightleftharpoons H\text{-}SO_3^-$ | | $6.55 \times 10^{2}$ | -2.82 | | 25 | Stromberg (1983) |
| $HO\text{-}SO_2^- \rightleftharpoons SO_3^{2-} + H^+$ | | $1.0 \times 10^{-7}$ | -7.00 | | 25 | Guthrie (1979) |
| $H\text{-}SO_3^- \rightleftharpoons SO_3^{2-} + H^+$ | | $2.51 \times 10^{-9}$ | -8.60 | | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY: METAL ION-S(IV) EQUILIBRIA

### TABLE T11

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Ag^+ + SO_3{}^{2-} \rightleftharpoons AgSO_3^+$ | 0 | $3.98 \times 10^5$ | -5.6 | | 25 | Smith & Martell (1976) |
| $Hg^{2+} + 2SO_3{}^{2-} \rightleftharpoons Hg(SO_3)_2^{2-}$ | 1.0 | $1.26 \times 10^{24}$ | -24.1 | | 25 | Ibid. |
| $Cu^+ + SO_3{}^{2-} \rightleftharpoons CuSO_3^-$ | 1.0 | $6.31 \times 10^7$ | -7.8 | | 25 | Ibid. |
| $Cu^+ + 2SO_3{}^{2-} \rightleftharpoons Cu(SO_3)_2^{3-}$ | 1.0 | $5.01 \times 10^8$ | -8.7 | | 25 | Ibid. |
| $Cd^{2+} + 2SO_3{}^{2-} \rightleftharpoons Cd(SO_3)_2^{2-}$ | 1.0 | $1.58 \times 10^4$ | -4.2 | | 25 | Ibid. |
| $Ce^{3+} + SO_3{}^{2-} \rightleftharpoons CeSO_3^+$ | 0 | $1.0 \times 10^8$ | -8.0 | | 25 | Ibid. |
| $UO_2^{2+} + SO_3{}^{2-} \rightleftharpoons UO_2SO_3^\circ$ | 1.0 | $2.0 \times 10^5$ | -5.3 | | 25 | Ibid. |
| $CaSO_3(s) \rightleftharpoons Ca^{2+} + SO_3{}^{2-}$ | 0 | $3.16 \times 10^{-7}$ | 6.5 | | 25 | Ibid. |
| $CH_3Hg^+ + SO_3{}^{2-} \rightleftharpoons CH_3HgSO_3^-$ | 0.1 | $1.26 \times 10^8$ | -8.1 | | 20 | Ibid. |
| $Fe^{2+} + HSO_3^- \rightleftharpoons FeHSO_3^+$ | 1.0 | $3.98 \times 10^1$ | -1.6 | | 25 | Kao (1979) |
| $Fe^{2+} + SO_3{}^{2-} \rightleftharpoons FeSO_3^\circ$ | 1.0 | $7.94 \times 10^5$ | -5.9 | + 60. | 25 | Ibid. |
| $Fe^{3+} + HSO_3^- \rightleftharpoons FeHSO_3{}^{2+}$ | 1.0 | $7.94 \times 10^1$ | -1.9 | | 25 | Ibid. |
| $Fe^{3+} + SO_3{}^{2-} \rightleftharpoons FeSo_3^+$ | 1.0 | $1.58 \times 10^7$ | -7.2 | -179.15 | 25 | Ibid. |

THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
S(VI) EQUILIBRIA
TABLE T12

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 0 | $1.02 \times 10^{-2}$ | 1.99 | -22.57 | 25 | Smith & Martell (1976) |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 0.1 | $2.82 \times 10^{-2}$ | 1.55 | | 25 | Ibid. |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 0.5 | $4.79 \times 10^{-2}$ | 1.32 | | 25 | Ibid. |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 1.0 | $7.94 \times 10^{-2}$ | 1.10 | -23.41 | 25 | Ibid. |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 2.0 | $9.77 \times 10^{-2}$ | 1.01 | | 25 | Ibid. |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 3.0 | $1.23 \times 10^{-1}$ | 0.91 | | 25 | Ibid. |
| $NH_4^+ + SO_4^{2-} \rightleftharpoons NH_4SO_4^-$ | 0 | $1.29 \times 10^{1}$ | -1.11 | | 18 | Ibid. |
| $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4^\circ$ | 0 | $1.70 \times 10^{2}$ | -2.23 | 5.85 | 25 | Ibid. |
| $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4^\circ$ | 0 | $2.04 \times 10^{2}$ | -2.31 | 6.69 | 25 | Ibid. |
| $CaSO_4(s) \rightleftharpoons Ca^{2+} + SO_4^{2-}$ | 0 | $2.40 \times 10^{-5}$ | 4.62 | 1.25 | 25 | Ibid. |
| $Mn^{2+} + SO_4^{2-} \rightleftharpoons MnSO_4$ | 0 | $1.82 \times 10^{2}$ | -2.26 | 8.78 | 25 | Ibid. |
| $Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4^\circ$ | 0 | $1.58 \times 10^{2}$ | -2.20 | 6.68 | 25 | Ibid. |
| $Co^{2+} + SO_4^{2-} \rightleftharpoons CoSO_4^\circ$ | 0 | $2.29 \times 10^{2}$ | -2.36 | 5.85 | 25 | Ibid. |
| $Ni^{2+} + SO_4^{2-} \rightleftharpoons NiSO_4^\circ$ | 0 | $2.09 \times 10^{2}$ | -2.32 | 6.27 | 25 | Ibid. |
| $Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4^\circ$ | 0 | $2.29 \times 10^{2}$ | -2.36 | 8.79 | 25 | Ibid. |
| $Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$ | 0 | $1.10 \times 10^{4}$ | -4.04 | 25.08 | 25 | Ibid. |
| $Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4^\circ$ | 0 | $5.62 \times 10^{2}$ | 2.75 | | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; CARBONYL BISULFITE ADDUCTS

### TABLE T13

REACTIONS:

$RCHO + H_2O \rightleftharpoons RCH(OH)_2$

$RCHO + HSO_3^- \rightleftharpoons RHC(OH)SO_3^-$

$R_1R_2C{=}O + HSO_3^- \rightleftharpoons R_1R_2C(OH)SO_3^-$

| Carbonyl | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $CH_2O$ | | $7.5 \times 10^4$ | -4.88 | -51.41 | 25 | Dasgupta el al. (1980) |
| $CH_2O$ | | $8.33 \times 10^6$ | -6.92 | | 25 | Skrabal & Skrabal (1936) |
| $C_6H_5CHO$ | | $1.02 \times 10^4$ | -4.01 | | 21° | Stewart & Donnally (1932) |
| $CH_2{=}CHCHO$ | | | | | | Finch (1962) |
| furfural | | $1.67 \times 10^3$ | -3.22 | | 25 | Hopner (1947) |
| $CH_3CHO + H_2O \rightleftharpoons CH_3HC(OH)_2$ | | 1.45 | -0.16 | | 25 | Bell (1966) |
| $CH_3CH_2CHO$ | .01 | $1.2 \times 10^4$ | -4.08 | - 2.65 | 20 | Gubareva (1947) |
| $CH_3CH_2CHO$ | .01 | $1.3 \times 10^4$ | -4.11 | - 2.65 | 0 | Ibid. |
| $CH_3(CH_2)_2CHO$ | .01 | $2.8 \times 10^4$ | -4.45 | -31.30 | 20 | Ibid. |
| $CH_3(CH_2)_2CHO$ | .01 | $7.2 \times 10^4$ | -4.86 | -31.30 | 0 | Ibid. |
| $CH_3(CH_2)_5CHO$ | .01 | $4.8 \times 10^3$ | -3.68 | + 5.22 | 20 | Ibid. |
| $CH_3(CH_2)_5CHO$ | .01 | $4.1 \times 10^3$ | -3.61 | + 5.22 | 0 | Ibid. |
| $(CH_3)_2C{=}O$ | .05 | $2.9 \times 10^2$ | 2.46 | -33.21 | 20 | Ibid. |
| $(CH_3)_2C{=}O$ | .05 | $7.9 \times 10^2$ | 2.90 | -33.21 | 0 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; CARBONYL BISULFITE ADDUCTS (cont.)

### TABLE T14

REACTIONS:

$$RCHO + HSO_3^- \rightleftharpoons RHC(OH)SO_3^-$$

$$R_1R_2C{=}O + HSO_3^- \rightleftharpoons R_1R_2C(OH)SO_3^-$$

| Carbonyl | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2CH_3$ | 0.05 | $0.6 \times 10^2$ | 1.79 | 32.50 | 20 | Ibid. |
| $CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2CH_3$ | 0.05 | $1.6 \times 10^2$ | 2.20 | 32.50 | 0 | Ibid. |
| $CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}COOC_2H_5$ | 0.01 | $0.9 \times 10^2$ | 1.95 | 45.00 | 20 | Ibid. |
| $CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2COOC_2H_5$ | 0.01 | $3.5 \times 10^2$ | 2.54 | 45.00 | 20 | Ibid. |
| $C_6H_5CHO$ | | $1.41 \times 10^4$ | 4.15 | 73.99 | 13 | Sousa & Margerum (1960a, b) |
| $C_6H_5CHO$ | | $4.74 \times 10^3$ | 3.68 | 73.99 | 23 | Ibid. |
| $C_6H_5CHO$ | | $1.85 \times 10^3$ | 3.27 | 73.99 | 33 | Ibid. |
| p-Cl-ϕ-CHO | 1.0 | $1.14 \times 10^4$ | 4.06 | ——— | 25 | Sander & Jencks (1968) |
| $NH_2NH\underset{\underset{O}{\|}}{C}NH_2$ | 1.0 | $1.4 \times 10^7$ | 7.15 | ——— | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
## HYDRATION OF ALDEHYDES
## TABLE T15

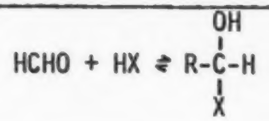
REACTION; $RCHO + H_2O \rightleftharpoons RCH(OH)_2$

| Aldehyde | $\mu$ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| HCHO | | $1.82 \times 10^3$ | -3.26 | -33.40 | 25 | LeHenaff (1968) |
| $CH_3CHO$ | | 1.05 | -0.02 | -21.32 | 25 | Ibid. |
| $CH_3CH_2CHO$ | | 0.85 | 0.07 | -24.24 | 25 | Ibid. |
| $CH_3(CH_2)_2CHO$ | | 0.65 | 0.19 | -26.33 | 25 | Ibid. |
| $ClCH_2CHO$ | | 28.57 | -1.46 | ——— | 25 | Ibid. |
| $(CH_3)_2CHCHO$ | | 0.61 | 0.22 | -22.57 | 25 | Ibid. |
| $(CH_3)_3CCHO$ | | 0.23 | 0.64 | -18.39 | 25 | Ibid. |
| $Cl_3CCHO$ | | $2.86 \times 10^4$ | -4.46 | -58.5 | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; NUCLEOPHILIC ADDITIONS TO HCHO

### TABLE T16

Reaction:



$$\mathrm{HCHO + HX \rightleftharpoons R\text{-}\overset{\displaystyle OH}{\underset{\displaystyle X}{C}}\text{-}H}$$

| Nucleophile | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| methylamine | | $3.4 \times 10^6$ | -6.53 | | 25 | LeHanaff (1965) |
| ethylamine | | $3.9 \times 10^6$ | -6.59 | | 25 | Sander & Jencks (1968) |
| urea | | $5.8 \times 10^4$ | -4.76 | | 25 | Ibid. |
| β-mercaptoethanol | | $1.4 \times 10^6$ | -6.15 | | 25 | Kallen & Jencks (1966) |
| $H_2O$ | | $2.28 \times 10^3$ | -3.36 | | 25 | Bell & Evans (1966) |
| $H_2O_2$ | | $3.5 \times 10^4$ | -4.54 | | 25 | Dunicz et al. (1951) |
| thioglycolate | | $1.1 \times 10^6$ | -6.04 | | 25 | LeHanaff (1966) |
| $H_2O$ | | $3.95 \times 10^4$ | -4.60 | +33.44 | 25 | Buschmann et al. (1980) |
| $H_2O$ | | $1.82 \times 10^3$ | -3.26 | | 25 | Bell (1966) |
| $H_2O_2$ | | $7.01 \times 10^3$ | -3.85 | | 25 | Marklund (1971) |
| $HOCH_2O\text{-}OH$ | | $7.78 \times 10^2$ | -2.89 | | 25 | Marklund (1971) |

### THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; IRON(II)/IRON(III)

### TABLE T17

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $\gamma\text{-FeOOH} + H_2O \rightleftharpoons Fe^{3+} + 3OH^-$ | 0 | $3.16 \times 10^{-42}$ | 41.5 | | 25 | Morel (1983) |
| $\text{am-Fe(OH)}_3 \rightleftharpoons Fe^{3+} + 3OH^-$ | 0 | $1.58 \times 10^{-39}$ | 38.8 | | 25 | Ibid. |
| $1/2\alpha\text{-}Fe_2O_3 + 3/2H_2O \rightleftharpoons Fe^{3+} + 3OH^-$ | 0 | $2.00 \times 10^{-43}$ | 42.7 | | 25 | Ibid. |
| $1/4[2FeO\cdot SiO_2] + H^+ \rightleftharpoons 1/2Fe^{2+} + 1/4H_2SiO_3 + 1/4H_2O$ | 0 | $1.62 \times 10^{4}$ | - 4.21 | | 25 | Delany & Helgeson (1978) |
| $Fe_3(PO_4)_2\cdot 8H_2O \rightleftharpoons 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$ | 0 | $1.0 \times 10^{-36}$ | 36.0 | | 25 | Smith & Martell (1976) |
| $FePO_4\cdot 2H_2O \rightleftharpoons Fe^{3+} + PO_4^{3-} + 2H_2O$ | 0 | $3.98 \times 10^{-27}$ | 26.4 | | 25 | Ibid. |
| $1/4[CaO\cdot FeO\cdot 2SiO_2] + H^+ \rightleftharpoons 1/4Ca^{2+} + 1/4Fe^{2+} + 1/2H_2SiO_3$ | 0 | $3.98 \times 10^{4}$ | - 4.6 | | 25 | Helgeson et al. (1978) |
| $FeOH^+ \rightleftharpoons Fe^{2+} + OH^-$ | 0 | $3.16 \times 10^{-5}$ | 4.5 | - 8.36 | 25 | Smith & Martell (1976) |
| $Fe(OH)_2^+ \rightleftharpoons Fe^{3+} + 2OH$ | 0 | $5.01 \times 10^{-23}$ | 22.3 | | 25 | Baes & Mesmer (1976) |
| $Fe(OH)_4^- \rightleftharpoons Fe^{3+} + 4OH^-$ | 0 | $3.98 \times 10^{-35}$ | 34.4 | | 25 | Ibid. |
| $Fe_2(OH)_2{}^{4+} \rightleftharpoons 2Fe^{3+} + 2OH^-$ | 0 | $7.94 \times 10^{-26}$ | 25.1 | -67.72 | 25 | Ibid. |
| $Fe_3(OH)_4{}^{5+} \rightleftharpoons 3Fe^{3+} + 4OH^-$ | 0 | $2.0 \times 10^{-50}$ | 49.7 | -158.84 | 25 | Ibid. |
| $Fe^{3+} + S_2O_3{}^{2-} \rightleftharpoons FeS_2O_3{}^+$ | 0 | $2.0 \times 10^{3}$ | - 3.3 | | 25 | Morel (1983) |
| $Fe^{3+} + HSiO_3^- \rightleftharpoons FeHSiO_3{}^{2+}$ | 0.1 | $7.94 \times 10^{8}$ | - 8.9 | 16.72 | 25 | Smith & Martell (1976) |

### THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; IRON(II)/IRON(III)

### TABLE T18

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Fe^{3+} + CH_3CO_2^- \rightleftharpoons FeCH_3CO_2{}^{2+}$ | 0 | $1.0 \times 10^4$ | - 4.0 | | 25 | Smith & Martell (1976) |
| $Fe^{3+} + 2(CH_3CO_2^-) \rightleftharpoons Fe(CH_3CO_2)_2^+$ | 0 | $3.98 \times 10^7$ | - 7.6 | | 25 | Ibid. |
| $Fe^{3+} + 3(CH_3CO_2^-) \rightleftharpoons Fe(CH_3CO_2)_3^\circ$ | 0 | $3.98 \times 10^9$ | - 9.6 | | 25 | Ibid. |
| $Fe^{2+} + CH_3CO_2^- \rightleftharpoons FeCH_3CO_2^+$ | 0 | $2.51 \times 10^1$ | - 1.4 | | 25 | Ibid. |
| $Fe^{3+} + HCO_2^- \rightleftharpoons FeHCO_2{}^{2+}$ | 0 | $1.26 \times 10^3$ | - 3.1 | | 25 | Ibid. |
| $3Fe^{3+} + 6HCO_2^- + 2OH^- \rightleftharpoons Fe_3(OH)_2(HCO_2)_6^+$ | 1.0 | $7.94 \times 10^{19}$ | -19.9 | | 20 | Ibid. |
| $Fe^{3+} + CH_3CH_2O_2^- \rightleftharpoons FeC_2H_5O_2{}^{2+}$ | 1.0 | $2.51 \times 10^3$ | - 3.4 | | 20 | Ibid. |
| $Fe^{3+} + (CH_3)_2CHCO_2 \rightleftharpoons Fe(CH_3)_2CHCO_2{}^{2+}$ | 1.0 | $3.98 \times 10^3$ | - 3.6 | | 20 | Ibid. |
| $Fe^{2+} + HOCH_2CO_2^- \rightleftharpoons Fe(HOCH_2CO_2)^+$ | 1.0 | $2.00 \times 10^1$ | - 1.3 | | 20 | Ibid. |
| $Fe^{3+} + HOCH_2CO_2^- \rightleftharpoons Fe(HOCH_2CO_2)^+$ | 1.0 | $7.94 \times 10^2$ | - 2.9 | | 20 | Ibid. |
| $Fe^{2+} + 2HSCH_2CO_2^- \rightleftharpoons Fe(HSCH_2CO_2)^\circ$ | 0 | $8.32 \times 10^{10}$ | -10.92 | | 25 | Ibid. |
| $Fe^{3+} + F^- \rightleftharpoons FeF^{2+}$ | 0 | $1.0 \times 10^6$ | - 6.0 | 9.61 | 25 | Ibid. |
| $Fe^{3+} + 2F^- \rightleftharpoons FeF_2{}^+$ | 0 | $3.98 \times 10^{10}$ | -10.6 | 14.63 | 25 | Ibid. |
| $Fe^{3+} + 3F^- \rightleftharpoons FeF_3{}^\circ$ | 0 | $5.01 \times 10^{13}$ | -13.7 | 18.39 | 25 | Ibid. |
| $Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$ | 0 | $3.16 \times 10^1$ | - 1.5 | 23.41 | 25 | Ibid. |
| $Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+$ | 0 | $1.35 \times 10^2$ | 2.13 | | 25 | Ibid. |

### THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; IRON(II)/IRON(III)

### TABLE T19

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Fe^{2+} + HPO_4{}^{2-} \rightleftharpoons FeHPO_4^\circ$ | 0 | $3.98 \times 10^3$ | -3.60 |  | 25 | Smith & Martell (1976) |
| $Fe^{2+} + H_2PO_4^- \rightleftharpoons FeH_2PO_4^+$ | 0 | $5.01 \times 10^2$ | -2.70 |  | 25 | Ibid. |
| $Fe^{3+} + HPO_4{}^{2-} \rightleftharpoons FeHPO_4^+$ | 0.5 | $2.0 \times 10^8$ | -8.30 |  | 25 | Ibid. |
| $Fe^{3+} + H_2PO_4^- \rightleftharpoons FeH_2PO_4{}^{2+}$ | 0.5 | $2.95 \times 10^3$ | -3.47 |  | 25 | Ibid. |
| $FeCO_3 \rightleftharpoons Fe^{2+} + CO_3{}^{2-}$ | 0 | $2.09 \times 10^{-11}$ | 10.68 |  | 25 | Ibid. |
| $Fe^{3+} + Br^- \rightleftharpoons FeBr^{2+}$ | 0 | 3.98 | -0.6 | 25.08 | 25 | Ibid. |
| $Fe^{3+} + NO_3^- \rightleftharpoons FeNO_3{}^{2+}$ | 0 | 10 | -1.0 | -37.62 | 25 | Ibid. |
| $Fe^{3+} + HO_2^- \rightleftharpoons FeO_2H^{2+}$ | 0.1 | $2.04 \times 10^9$ | -9.31 | 8.36 | 20 | Ibid. |
| $Fe^{3+} + {}^-O_2CH_2OCH_2CO_2^- \rightleftharpoons$ | 0.5 |  | -5.04 |  | 25 | Ibid. |
| $Fe^{2+} + {}^-O_2CH_2OCH_2CO_2^- \rightleftharpoons$ | 0.1 |  | -2.56 |  | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; Mn(II)/Mn(III)/Mn(IV)

### TABLE T20

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Mn(OH)_2(s) \rightleftharpoons Mn^{2+} + 2OH^-$ | 0 | | 12.8 | | 25 | Morel (1983) |
| $MnOH^+ \rightleftharpoons Mn^{2+} + OH^-$ | 0 | | 3.4 | | 25 | Ibid. |
| $MnCO_3(s) \rightleftharpoons Mn^{2+} + CO_3{}^{2-}$ | 0 | | 10.4 | | 25 | Smith & Martell (1976) |
| $MnOH^{2+} \rightleftharpoons Mn^{3+} + OH^-$ | 0 | | 14.4 | -33.4 | 25 | Ibid. |
| $Mn(OH)_4{}^{2-} \rightleftharpoons Mn^{2+} + 4OH^-$ | 0 | | 7.7 | | 25 | Ibid. |
| $Mn_2OH^{3+} \rightleftharpoons 2Mn^{2+} + OH^-$ | 0 | | 3.4 | | 25 | Ibid. |
| $Mn_2(OH)_3^+ \rightleftharpoons 2Mn^{2+} + 3OH^-$ | 0 | | 18.1 | | 25 | Ibid. |
| $Mn^{2+} + SO_4{}^{2-} \rightleftharpoons MnSO_4^\circ$ | 0 | | - 2.32 | 8.78 | 25 | Ibid. |
| $Mn^{2+} + SO_4{}^{2-} \rightleftharpoons MnS_2O_3^\circ$ | 0 | | - 1.95 | 2.09 | 25 | Ibid. |
| $Mn^{2+} + NO_3^- \rightleftharpoons MnNO_3^+$ | 0 | | - 0.2 | | 25 | Ibid. |
| $Mn^{2+} + 2NO_3^- \rightleftharpoons Mn(NO_3)_2^\circ$ | 0 | | - 0.6 | | 25 | Ibid. |
| $Mn^{3+} + F^- \rightleftharpoons MnF^{2+}$ | 2.0 | | - 5.65 | | 25 | Ibid. |
| $Mn^{2+} + F^- \rightleftharpoons MnF^+$ | 1.0 | | - 0.7 | | 25 | Ibid. |
| $Mn^{2+} + Cl^- \rightleftharpoons MnCl^+$ | 1.0 | | -0.04 | | 25 | Ibid. |
| $Mn^{2+} + HCO_3^- \rightleftharpoons MnHCO_3^+$ | 0 | | -1.8 | | 25 | Ibid. |
| $Mn^{2+} + NH_3 \rightleftharpoons MnNH_3{}^{2+}$ | 0 | | -1.0 | | 25 | Ibid. |
| $Mn^{2+} + CH_3CO_2^- \rightleftharpoons Mn(CH_3CO_2)^+$ | 0 | | -1.4 | | 25 | Ibid. |
| $Mn^{2+} + 2NH_3 \rightleftharpoons Mn(NH_3)_2{}^{2+}$ | 0 | | -1.5 | | 25 | Ibid. |

### THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; ACID-BASE

### TABLE T21

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $H_2S \rightleftharpoons H^+ + HS^-$ | 0 | | 7.02 | -22.15 | 25 | Smith & Martell (1976) |
| $HS^- \rightleftharpoons H^+ + S^{2-}$ | 0 | | 13.9 | -50.16 | 25 | Ibid. |
| $H_2S_2O_3 \rightleftharpoons H^+ + HS_2O_3^-$ | 0 | | 0.6 | | 25 | Ibid. |
| $HS_2O_3^- \rightleftharpoons H^+ + S_2O_3^{2-}$ | 0 | | 1.6 | | 25 | Ibid. |
| $HF \rightleftharpoons H^+ + F^-$ | 0 | | 3.17 | 13.38 | 25 | Ibid. |
| $HCO_2H \rightleftharpoons HCO_2^- + H^+$ | 0 | | 3.75 | 0.17 | 25 | Martell & Smith (1977) |
| $CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$ | 0 | | 4.76 | 0.42 | 25 | Ibid. |
| $C_2H_5CO_2H \rightleftharpoons C_2H_5CO_2^- + H^+$ | 0 | | 4.87 | 0.84 | 25 | Ibid. |
| butanoic acid | 0 | | 4.82 | 2.97 | 25 | Ibid. |
| isobutyric acid | 0 | | 4.85 | 3.22 | 25 | Ibid. |
| pentanoic acid | 0 | | 4.84 | 2.88 | 25 | Ibid. |
| pivalic acid | 0 | | 5.03 | 3.01 | 25 | Ibid. |
| phenylacetic acid | 0 | | 4.31 | | 25 | Ibid. |
| vinylacetic acid | 0 | | 3.34 | | 25 | Ibid. |
| crotonic acid | 0 | | 4.69 | | 25 | Ibid. |
| benzoic acid | 0 | | 4.20 | - 0.46 | 25 | Ibid. |
| acrylic acid | 0 | | 4.26 | 1.88 | 25 | Ibid. |

## THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
## ACID -BASE
## TABLE T22

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $H_2O_2 \rightleftharpoons HO_2^- + H^+$ | 0 |  | 11.65 | -30.93 | 25 | Smith & Martell (1976) |
| $H_2O_2 \rightleftharpoons HO_2^- + H^+$ | 3.0 |  | 12.13 |  | 5 | Ibid. |
| $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ | 0 |  | 6.35 | - 8.36 | 25 | Ibid. |
| $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ | 0 |  | 10.33 | -14.63 | 25 | Ibid. |
| $H_4SiO_4 \rightleftharpoons H_3SiO_3^- + H^+$ | 0 |  | 9.86 | -20.90 | 25 | Ibid. |
| $H_3SiO_4^- \rightleftharpoons H^+ + H_2SiO_4^{2-}$ | 0 |  | 13.10 | -41.80 | 25 | Ibid. |
| $am\text{-}SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$ | 1.0 |  | 2.74 |  | 25 | Ibid. |
| $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | 0 |  | 3.15 | - 8.36 | 25 | Ibid. |
| $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | 0.5 |  | 2.94 |  | 25 | Ibid. |
| $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | 1.0 |  | 3.00 |  | 25 | Ibid. |
| $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | 2.0 |  | 3.24 |  | 25 | Ibid. |
| $NH_4^+ \rightleftharpoons H^+ + NH_3$ | 0 |  | 9.24 | -52.04 | 25 | Ibid. |
| $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ | 0 |  | 12.35 | -14.63 | 25 | Ibid. |
| $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ | 0 |  | 7.20 | - 3.34 | 25 | Ibid. |
| $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ | 0 |  | 2.15 | - 8.99 | 25 | Ibid. |
| $H_2O \rightleftharpoons H^+ + OH^-$ | 0 |  | 13.997 | -55.76 | 25 | Ibid. |

THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
ACID-BASE
TABLE T23

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^-$ | 0 | | 33.5 | | 25 | Morel (1983) |
| $Al(OH)^{2+} \rightleftharpoons Al^{3+} + OH^-$ | 0 | | 9.0 | | 25 | |
| $Al(OH)_2^+ \rightleftharpoons Al^{3+} + 2OH^-$ | 0 | | 18.7 | | 25 | |
| $Al(OH)_3^\circ \rightleftharpoons Al^{3+} + 3OH^-$ | 0 | | 27.0 | | 25 | |
| $Al(OH)_4^- \rightleftharpoons Al^{3+} + 4OH^-$ | 0 | | 33.0 | | 25 | |
| $Al_2(OH)_2^{4+} \rightleftharpoons 2Al^{3+} + 2OH^-$ | 0 | | 20.3 | | 25 | |
| $Al_3(OH)_4^{5+} \rightleftharpoons 3Al^{3+} + 4OH^-$ | 0 | | 42.1 | | 25 | |
| $H_2SO_5 \rightleftharpoons H^+ + HSO_5^-$ | 0 | | 1.0 | | 25 | Perrin (1982) |
| $HSO_5^- \rightleftharpoons H^+ + SO_5^{2-}$ | 0.2 | | 9.3 | | 25 | Ibid. |
| $HOONO \rightleftharpoons H^+ + {}^-OONO$ | | | <6 | | 23 | Ibid. |
| $Cu(OH)_2(s) \rightleftharpoons Cu^{2+} + 2OH^-$ | 0 | | 19.4 | | 25 | Morel (1983) |
| $Cu(OH)_2^{2+} \rightleftharpoons Cu^{2+} + 4OH^-$ | 0 | | 16.4 | | 25 | |
| $Cu_2(OH)_2^{2+} \rightleftharpoons 2Cu^{2+} + 2OH^-$ | 0 | | 17.6 | | 25 | Smith & Martell (1976) |
| $Cu(OH)_3^- \rightleftharpoons Cu^{2+} + 3OH^-$ | 1.0 | | 14.5 | | 25 | |
| $Cu(OH)_2^\circ \rightleftharpoons Cu^{2+} + 2OH^-$ | 1.0 | | 12.8 | | 25 | |
| $Cu(OH)^+ \rightleftharpoons Cu^{2+} + OH^-$ | 0 | | 6.3 | | 25 | |

THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; ACID-BASE
TABLE T24

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HO_2 \rightleftharpoons H^+ + O_2^-$ | | | 4.45 | | 23 | Perrin (1982) |
| $HO \rightleftharpoons H^+ + O^-$ | | | 11.9 | | 23 | Ibid. |
| $H_2N_2O_2 \rightleftharpoons HN_2O_2^- + H^+$ | 0 | | 7.21 | | 25 | |
| $HN_2O_2^- \rightleftharpoons N_2O_2{}^{2-} + H^+$ | 0 | | 11.54 | | 25 | |
| $HNO_3 \rightleftharpoons H^+ + NO_3^-$ | 0 | | - 1.37 | | 25 | Ibid. |
| $NH_2SO_3H \rightleftharpoons NH_2SO_3^- + H^+$ | 0 | | 0.99 | | 25 | Ibid. |
| $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ | | | - 3.00 | | 25 | Ibid. |
| $CH_3O\text{-}OH \rightleftharpoons CH_3O\text{-}O^- + H^+$ | | | 11.5 | | 20 | Serjeant & Dempsey (1979) |
| $CH_3SO_3H \rightleftharpoons CH_3SO_3^- + H^+$ | | | - 1.2 | | 25 | Ibid. |
| $HOCN_2CO_2H \rightleftharpoons HOCH_2CO_2^- + H^+$ | | | 3.831 | | 25 | Martell & Smith (1977) |
| $HOOCCOOH \rightleftharpoons H^+ + {}^-O_2CO_2H$ | 0 | | 1.25 | | 25 | Serjeant & Dempsey (1979) |
| ${}^-O_2CO_2H \rightleftharpoons H^+ + C_2O_4{}^{2-}$ | 0 | | 4.26 | 6.69 | 25 | |
| $CH_3CHO \rightleftharpoons CH_3CO^- + H^+$ | | | 13.57 | | 25 | Serjeant & Dempsey (1979) |
| $\phi\text{-}CHO \rightleftharpoons \phi\text{-}CO\text{-} + H^+$ | | | 14.9 | | 25 | Ibid. |
| α-hydroxy-α-(6-methyl-2-pyridyl)- | | | 4.83 ($pK_1$) | | 25 | Ibid. |
| methanesulfonic acid | | | 9.88 ($pK_2$) | | 25 | Ibid. |
| $CH_3\overset{OH}{C}HCO_2H \rightleftharpoons CH_3\overset{OH}{C}HCO_2^- + H+$ | 0 | | 3.86 | 0.33 | 25 | Martell & Smith (1977) |

## THERMOTHERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; Mn(II)/Cu(II)
### TABLE T25

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Mn^{2+} + CH_3\overset{\overset{OH}{\vert}}{C}HCO_2^- \rightleftharpoons Mn(CH_3\overset{\overset{OH}{\vert}}{C}HCO_2)^+$ | 0 | $2.69 \times 10^1$ | - 1.43 | | 25 | Martell & Smith (1977) |
| $Mn^{2+} + {}^-O_2CCH_2OCH_2CO_2^- \rightleftharpoons$ | 0.1 | $3.38 \times 10^2$ | - 2.53 | | 25 | Ibid. |
| $Mn^{2+} + CH_3\overset{\overset{O}{\Vert}}{C}CO_2^- \rightleftharpoons Mn(CH_3\overset{\overset{O}{\Vert}}{C}CO_2)$ | 0.1 | $1.82 \times 10^2$ | - 1.26 | | 25 | Ibid. |
| $Cu^{2+} + CO_3{}^{2-} \rightleftharpoons CuCO_3^\circ$ | 0 | $5.62 \times 10^6$ | - 6.75 | | 25 | Smith & Martell (1976) |
| $Cu^{2+} + 2CO_3{}^{2-} \rightleftharpoons Cu(CO_3)_2{}^{2-}$ | 0 | $8.32 \times 10^9$ | - 9.92 | | 25 | Ibid. |
| $CuCO_3(s) \rightleftharpoons Cu^{2+} + CO_3{}^{2-}$ | 0 | $2.34 \times 10^{-10}$ | 9.63 | | 25 | Ibid. |
| $Cu_2(OH)_2CO_3(s) \rightleftharpoons 2Cu^{2+} + 2OH^- + CO_3{}^{2-}$ | 0 | $1.58 \times 10^{-34}$ | 33.8 | | 25 | Ibid. |
| $Cu_3(OH)_2(CO_3)_2(s) \rightleftharpoons 3Cu^{2+} + 2OH^- + 2CO_3^{2-}$ | 0 | $1.10 \times 10^{-46}$ | 45.96 | | 25 | Ibid. |
| $Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4^\circ$ | 0 | $2.51 \times 10^2$ | - 2.4 | 8.78 | 25 | Ibid. |
| $Cu_4(OH)_6SO_4(s) \rightleftharpoons 4Cu^{2+} + 6OH^- + SO_4^{2-}$ | 0 | $2.51 \times 10^{-61}$ | 68.6 | 33.4 | 25 | Ibid. |
| $Cu^{2+} + F^- \rightleftharpoons CuF^+$ | 0 | $3.16 \times 10^1$ | - 1.5 | 4.18 | 25 | Morel (1983) |
| $Cu^{2+} + NH_3 \rightleftharpoons CuNH_3{}^{2+}$ | 0 | $1.10 \times 10^4$ | - 4.04 | -23.0 | 25 | Smith & Martell (1976) |
| $Cu^{2+} + 2NH_3 \rightleftharpoons Cu(NH_3)_2{}^{2+}$ | 0 | $2.95 \times 10^7$ | - 7.47 | -46.4 | 25 | Ibid. |
| $Cu^{2+} + 3NH_3 \rightleftharpoons Cu(NH_3)_3{}^{2+}$ | 0 | $1.86 \times 10^{10}$ | -10.27 | -69.4 | 25 | Ibid. |
| $Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4{}^{2+}$ | 0 | $5.62 \times 10^{11}$ | -11.75 | -92.0 | 25 | Ibid. |

### THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY; Cu(II)

### TABLE T26

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $Cu^{2+} + HPO_4^- \rightleftharpoons CuHPO_4^+$ | 0.15 | $2.0 \times 10^3$ | - 3.3 | | 37 | Smith & Martell (1976) |
| $Cu^{2+} + H_2PO_4^- \rightleftharpoons CuH_2PO_4^\circ$ | 0.15 | $2.0 \times 10^1$ | - 1.3 | | 37 | Ibid. |
| $Cu^{2+} + NH_2(CH_2)_2NH_2 \rightleftharpoons$ | 0 | $3.16 \times 10^{10}$ | -10.5 | | 25 | Morel (1983) |
| $Cu^{2+} + 2\ NH_2(CH_2)_2NH_2 \rightleftharpoons$ | 0 | $3.98 \times 10^{19}$ | -19.6 | | 25 | Ibid. |
| $Cu^{2+} + OH^- + NH_2(CH_2)_2NH_2 \rightleftharpoons$ | 0 | $6.31 \times 10^{11}$ | -11.8 | | 25 | Ibid. |
| $Cu^{2+} + HOCH_2CO_2^- \rightleftharpoons CuHOCH_2CO_2^+$ | 0 | $7.94 \times 10^2$ | 2.90 | | 25 | Martell & Smith (1977) |
| $Cu^{2+} + 2(HOCH_2CO_2^-) \rightleftharpoons Cu(HOCH_2CO_2)_2^\circ$ | 0 | $4.57 \times 10^4$ | 4.66 | | 25 | Ibid. |
| $Cu^{2+} + 2(CH_3CO_2^-) \rightleftharpoons Cu(CH_3CO_2^-)_2$ | 0 | $4.27 \times 10^3$ | 3.63 | 5.85 | 25 | Ibid. |
| $Cu^{2+} + CH_3CO_2^- \rightleftharpoons CuCH_3CO_2^+$ | 0 | $1.58 \times 10^2$ | 2.2 | 4.18 | 25 | Ibid. |
| $Cu^{2+} + HCO_2^- \rightleftharpoons CuHCO_2^+$ | 0 | $1.0 \times 10^2$ | 2.0 | | 25 | Ibid. |
| $Cu^{2+} + 2HCO_2^- \rightleftharpoons Cu(HCO_2)^\circ$ | 5.0 | $4.27 \times 10^2$ | 2.63 | | 25 | Ibid. |
| $Cu^{2+} + 3HCO_2^- \rightleftharpoons Cu(HCO_2)^-$ | 5.0 | $1.0 \times 10^3$ | 3.00 | | 25 | Ibid. |
| $Cu^{2+} + C_2H_5CO_2^- \rightleftharpoons Cu(C_2H_5CO_2)^+$ | 0 | $1.66 \times 10^2$ | 2.22 | | 25 | Ibid. |
| $Cu^{2+} + 2C_2H_5CO_2^- \rightleftharpoons Cu(C_2H_5CO_2)_2^\circ$ | 3.0 | $1.0 \times 10^3$ | 3.00 | | 25 | Ibid. |
| $Cu^{2+} + C_3H_7CO_2^- \rightleftharpoons Cu(C_3H_7CO_2)^+$ | 0 | $1.38 \times 10^2$ | 2.14 | | 25 | Ibid. |
| $Cu^{2+} + C_4H_9CO_2^- \rightleftharpoons Cu(C_4H_9CO_2)^+$ | 0 | $1.32 \times 10^2$ | 2.12 | | 25 | Ibid. |

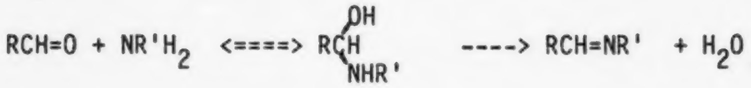
THERMODYNAMIC DATA: AQUEOUS-PHASE EQUILIBRIA RELEVANT TO DROPLET-PHASE CHEMISTRY;
ACID-BASE
TABLE T27

| Reaction | μ | K | pK | $\Delta H^\circ_{298}$ | T(°C) | Reference |
|---|---|---|---|---|---|---|
| $HO_2CH_2OCH_2CO_2H \rightleftharpoons$ | 0 | $1.07 \times 10^{-3}$ | 2.97 | 3.18 | 25 | Martell & Smith (1977) |
| $-O_2CH_2OCH_2CO_2H \rightleftharpoons$ | | $4.27 \times 10^{-5}$ | 4.37 | -1.59 | 25 | Martell & Smith (1977) |
| $NO_2CH_2CO_2H \rightleftharpoons NO_2CH_2CO_2^- + H^+$ | | $2.09 \times 10^{-2}$ | 1.68 | 4.18 | 18 | Ibid. |
| $CH_3HCNH_2SO_3^- \rightleftharpoons$ | | $8.51 \times 10^{-10}$ | 9.07 | | 25 | Serjeant & Dempsey (1979) |
| o-cresol $\rightleftharpoons$ | 0 | $4.79 \times 10^{-11}$ | 10.32 | | 25 | Ibid. |
| m-cresol $\rightleftharpoons$ | 0 | $7.94 \times 10^{-11}$ | 10.10 | | 25 | Ibid. |
| p-cresol $\rightleftharpoons$ | 0 | $5.25 \times 10^{-11}$ | 10.28 | | 25 | Ibid. |
| $CH_3(CH_2)_3CO_2H \rightleftharpoons$ | 0 | $1.45 \times 10^{-5}$ | 4.84 | 2.88 | 25 | Martell & Smith (1977) |
| $HC \equiv CCO_2H \rightleftharpoons$ | 0.1 | $1.29 \times 10^{-2}$ | 1.89 | 10.41 | 25 | Ibid. |

# APPENDIX C

## ALDEHYDE-AMMONIA ADDUCTS IN ATMOSPHERIC WATER DROPLETS

The reaction between amines and carbonyls is a well known organic reaction (7). Amines and ammonia are effective nucleophiles that add to the carbonyl group of aldehydes or ketones by the following general reaction.



$$RCH{=}O + NR'H_2 \Longleftrightarrow RC\overset{OH}{\underset{NHR'}{H}} \longrightarrow RCH{=}NR' + H_2O \qquad (1)$$

The addition products of ammonia and aldehydes are unstable and condense to polymeric products. Amines may add to aldehydes and then lose a water to form imines (the Schiff's base reaction). Schiff's bases of aliphatic amines and aldehydes are also unstable and polymerize to more complex products, however, when aromatic aldehydes or more complex amines react the products are often stable.

The reaction of ammonia with formaldehyde leads to the formation of hexamethylentetramine (also known as hexamine or urotropine), an important compound in manufacturing and pharmaceuticals (27). Synthesis of hexamine was first reported in 1859 by Butlerow (5). A variety of investigators have studied the kinetics and thermodynamics of the aldehyde ammonia reaction over the last century. However, our understanding of this reaction is still poor. The major points of agreement are that the reaction goes rapidly to completion when molar concentrations of reactants are mixed at high pH, and that semistable intermediates are formed with comparable rapidity. The kinetics and thermodynamics of this reaction at moderate concentrations and neutral to acidic pH are not well known. In addition, reactions between a variety of amines and aldehydes have been studied and some of these results can possibly be extrapolated to the formaldehyde ammonia reaction.

The recent finding that ammonia, formaldehyde, acetaldehyde, and perhaps some higher aldehydes are present in fog- and cloudwater at concentrations exceeding $10^{-3}$ $\underline{M}$ (8,15) suggests that the possibility of aldehyde-ammonia reactions should be considered in models of fog and cloudwater chemistry. Grosjean and Wright (8) suggest that aldehydes may react with ammonia or amines in the alkaline ice fogs of Alaska. At sites such as the San Joaquin Valley and eastern Los Angeles basin, where ammonia emissions are very high and aldehydes from hydrocarbon oxidation are present (12,15), this reaction could enhance the equilibrium concntrations of aldehyde and ammonia in the fog and cloud droplets. In this appendix the available literature on the aldehyde-ammonia reaction is reviewed and the its possible importance in the atmosphere is discussed.

## KINETIC EXPERIMENTS

The reaction of formaldehyde and ammonia has been studied by following the disappearance of reactants or formation of the product, hexamine. Most of the kinetic studies have been designed to determine the rate of hexamine formation and have been done at 0.1 $\underline{M}$ or greater concentrations. In many cases pH was not considered, however, at the high $NH_3$ concentrations used pH was near 10 - 11. As indicated in Table 1, the reported rate constants are generally low. Most studies have found that the rate is best described by an expression that is second order in formaldehyde and first order in ammonia.

Baur and Reutschi (3) determined ammonia in aliquots removed from the reaction mixture. Their observed rate constant was a factor of 4 less when ammonia was at a 4-fold excess than when $CH_2O$ and $NH_3$ were in a stoichiometric ratio. The equilibrium constant (as defined in Table 5.2), was $6.3 \times 10^{-11}$ $\underline{M}^{-5}$ at 298 K. The $[H^+]^4$ dependence makes hexamine very stable at high pH, however, stability decreases rapidly as pH is lowered. The value determined for H was 19.5 kcal $mole^{-1}$.

Bose (4) studied the formation of hexamine by following the disappearance of $CH_2O$. No information is given about pH in his experiment, so it must be assumed that the reaction was unbuffered. His data are given as half-lives for the reaction using different initial concentrations. The third order rate constants calculated from his half-lives (Table 1) are comparable to Baur and Reutschi. In addition, Bose observed that a significant amount of intermediate was formed, which hydrolyzed to equimolar $CH_2O$ and $NH_3$ by addition of dilute acid in the analytical procedure used.

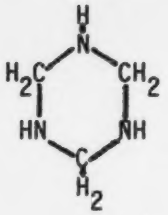
Ogata and Kawasaki (14,19) studied the $CH_2O$ - $NH_3$ reaction by following the disappearance of $CH_2O$. Their analytical procedure apparently did not hydrolyze $CH_2O$-$NH_3$ intermediates, which would account for the higher rate constants. Their study revealed that k had an an inverse dependence on $[H^+]$. The maximum in the rate constant at about pH 10 corresponds roughly to the $pK_a$ for ammonium. The measured rate constant in an unbuffered solution, which had an initial pH of 10.5 that decreased to 10.2, was considerably less than the rate constant in a buffered solution at the same, pH, but this discrepancy is not explained. They report no significant salt effect at pH 7.9. Contrary to other investigations they found a 2:1 ratio of $CH_2O$ to $NH_3$ in the intermediate. However, this ratio does not agree with the expected ratio for the intermediates they postulate.

In a kinetic study using a continuous-flow stirred tank reactor, Wood and Stevens (28) measured the rate of hexamine formation by following the loss of unhydrolyzable $CH_2O$. Their reaction appears to be in an unbuffered solution. Although they note a better fit to the data using fractional order, only the rate constants and activation parameters for the overall third order rate expression have been listed in Table 1. Without information on the pH of the solution their data cannot be used to calculate an equilibrium constant.

Two other studies (2,26) present kinetic information for the formation of hexamine. However, they fail to define how they derived the rate constants, making their results meaningless, except to confirm that the reaction is 3rd order. Winkler et al. (22,11) do not give any rate constants, but from their plots it is apparent that formation of hexamine is rapid. For initial concentrations of 0.3 $\underline{M}$ $CH_2O$ and 0.2 $\underline{M}$ $NH_3$, nearly quantitative formation of hexamine was obtained in 12 minutes at pH above 6. Slower rate and reduced yield were obtained at pH 4. They also observe that a significant amount of intermediate is formed. The rate curves for hexamine formed are less than the $CH_2O$ and $NH_3$ consumption by up to 8% based on yield of product. The formation of product was greatest when $CH_2O$ was in a 2-fold stoichiometric excess over $NH_3$. A significant induction period for hexamine formation is further evidence for the presence of an intermediate.

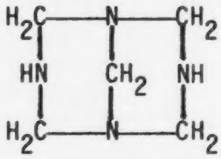
## REACTION INTERMEDIATES

Formation of tribenzoyl and trinitroso derivatives with benzoyl chloride and nitrous acid (19,23) and NMR spectra (18) indicate that 2,4,6-trialkyl-1,3,5-hexahydrotriazine (HHT) is the major species



HHT

formed initially when $CH_2O$ and $NH_3$ are mixed together. The lifetime for conversion of HHT to hexamine decreaes from days to minutes as pH is decreased. NMR spectra also indicate that 1,3,5,7-tetraazabicyclo-[3.3.1] nonane (TABN) is present in mixtures of $CH_2O$ and $NH_3$ (18).



TABN

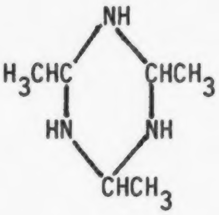
Ogata and Kawasaki (14,19) reported that the dibenzamide derivative with benzoyl chloride was formed as well; and was the exclusive product when $NH_3$ was in excess over $CH_2O$. UV spectra indicate that only amines are present in $CH_2O$-$NH_3$ solutions. Formation of HHT as a major intermediate is consistent with the majority of observations that the $CH_2O$:$NH_3$ ratio of the intermediate is 1:1.

The formation of triazines is observed for the other aldehydes as well (25). Nielsen et al. (16,17) prepared and isolated triazines for a series of aliphatic aldehydes. They observed that the analagous 1-amino-1-alkanols (alkanolamines or carbinolamines) could only be prepared at cold temperature. Infrared spectra of the amino-alkanols indicated presence of both carbonyl C=0 and imine C=N bonds indicating rapid dehydration and deamination. At room temperature they rapidly decomposed to the trimers (triazines) with the evolution of ammonia.

Table 2 and 3 present thermodynamic and kinetic data for reactions of higher aldehydes with ammonia or amines and formaldehyde with amines. Because the polymerization that proceeds in the $CH_2O-NH_3$ reaction is hindered for higher aldehydes and amines, the initial steps may be studied in isolation. Using NMR spectroscopy Hull et al. (10) determined the formation rate and equilibria for the reaction of $CH_3CHO$ and $NH_3$.

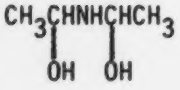
$$CH_3CHO + NH_3 \underset{k_{-1}}{\overset{k_1}{<====>}} CH_3CH(OH)NH_2 \underset{k_{-2}}{\overset{k_2}{<====>}} CH_3CH{=}NH + H_2O \qquad (2)$$

The cyclic trimer 2,4,6-trimethylhexahydro-s-triazine



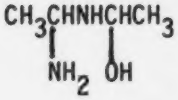
I

was identified as a major product, and its identification confirmed by infrared and mass spectrometry. However, its importance decreased with pH or reduced $[NH_3]$. At pH 10.6 about 65% of the methyl resonances could be accounted for by the trimer and only 5% as the aldehyde and its hydrate, while at pH 7.5 aldehyde and hydrate accounted for 80%. An equilibrium constant in terms of unhydrated aldehyde and free ammonia is given in Table 2. Because of the $NH_4^+ == NH_3 + H^+$ equilibria, the stability of the trimer decreases rapidly with pH. Other adducts besides trimer are indicated by separate methyl doublets in the NMR spectra. These are attributed to the following species.



$CH_3CH(OH)NHCH(OH)CH_3$

II



$CH_3CH(NH_2)NHCH(OH)CH_3$

III

Formation and decomposition of the trimer is slow on the NMR time scale as indicated by a distinct resonance line. Only the equilibria between aldehyde, carbinolamine, and imine ($k_{>1}$, $k_{>2}$) contribute to the observed NMR line broadening. The equilibria and rate constants calculated from NMR data are given in Tables 2 and 3. It is apparent that the rate constant for this initial step in the acetaldehyde ammonia reaction is more rapid than the overall rate constant for the formaldehyde ammonia reaction. Although, the stability of the carbinolamine is fairly small, the exponents on the reactants are not as large, so the concentration of complex may be higher.

Ogata and Kawasaki (19,20) conducted a study of ammonia addition to a series of aliphatic aldehydes using spectrophotometry. They claim that they have determined the rates of carbinolamine formation, but evidence to that effect is not conclusive. Hull et al. (10) note that Ogata and Kawasaki's rate constants are much slower than they observed. Thus Ogata and Kawasaki's data should be used with the caution that it may describe the overall rate of triazine formation. The rate constant for the reverse reaction was derived from the forward rate and equilibrium constant. When the observed rate constants are corrected for the acid-base and hydration equilibria of the reacting species, acid catalysis was apparent; the rate constant increases with $[H^+]$.

Decreasing concentration of free $NH_3$ with lower pH will offset the increase in rate constant. The negative dependence of forward rate constant on the length of the carbon chain is small. Somewhat larger increases in the reverse rate constant lead to a 10 fold decrease in the equilibrium constant from acetaldehyde to butyraldehyde. One would expect the analagous kinetic and thermodynamic constants for the $CH_2O$-$NH_3$ reaction to be comparable to the corresponding acetaldehyde-ammonia constants.

When amines react with aldehydes, polymeric products are not formed. Several studies of aldehye-amine reactions have indicated that the kinetics are complex and may involve acid and base catalysis because of the multiple acid-base equilibria for the reactants and products (1,6,13). Weak acids, HA, appear to facilitate proton rearrangement of the aldehyde-amine complex, making the forward reaction more stable (1). A number of linear relationships have been derived for equilibrium and rate constants of aldehyde-amine reactions. For formaldehyde and exocyclic aromatic amines, Abrams and Kallen (1) observed a linear relationship between the log of carbinolamine formation constant and the $pK_a$ of the amine; the slope was 0.04 for anilines and 0.16 for methylanilines. In a study of aliphatic amines and isobutyraldehyde, Hine and Via (9) observed a linear relationship of both rate and equilibrium constant and $pK_a$ of the amine; inclusion of a steric factor improved the fit of the equilibrium constants. Sander and Jencks (24) fit the equilibrium constant for the reaction of formaldehyde and 2 substituted aromatic aldehydes with a series of amines to an affinity constant; Formaldehyde had the highest equilibrium constant for each amine. Hull et al. noted that their equilibrium constant for the acetaldehyde-ammonia reaction would fit on Hine and Via's linear free energy relationship (LFER) for aliphatic amines. Extrapolation of kinetic and thermodynamic data for higher aldehydes and amines must be done cautiously because both $CH_2O$ and $NH_3$ are quite different from their homologs and the formaldehyde-ammonia reaction is subject to greater polymerization.

## MECHANISM

A number of mechanisms have been proposed to account for the kinetic and ancillary data described above in the reaction between formaldehyde and ammonia. The sequence of reactions presented here combines features of a number of proposed mechanisms, following Ogata and Kawasaki (14,19) and Nielsen et al. (18) most closely.

The unhydrated aldehyde and free $NH_3$ are considered to be the reactive species. The following prequilibria explain the observed pH dependence of the reaction rate.

$$CH_2(OH)_2 <===> CH_2O + H_2O \qquad (3)$$

$$NH_4^+ <===> NH_3 + H^+ \qquad (4)$$

There appears to be consensus that the first addition of ammonia to formaldehyde and the subsequent dehydration is rapid. This step is on the order of $10^4$ for acetaldehyde plus ammonia. The second addition of aldehyde to form a dimethylolamine is considered to be the rate limiting step, which accounts for the overall 3rd order of the reaction.

$$CH_2O + NH_3 <===> \underset{\textbf{IV}}{H_2NCH_2OH} \qquad (5)$$

$$H_2NCH_2OH \Longleftrightarrow \underset{\mathbf{V}}{HN{=}CH_2} + H_2O \qquad (6)$$

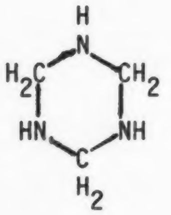
$$H_2NCH_2OH + CH_2O \Longleftrightarrow \underset{\mathbf{VI}}{HN(CH_2OH)_2} \qquad (7)$$

$$H_2NCH_2OH + NH_3 \Longleftrightarrow \underset{\mathbf{VII}}{H_2NCH_2NH_2} + H_2O \qquad (8a)$$

$$\mathbf{V} + NH_3 \Longleftrightarrow \mathbf{VII} \qquad (8b)$$

For the reaction of ammonia with formaldehyde and other small aldehydes the products IV and V can not be isolated; they condense to form triazines in a sequence such as the following. Other sequences leading to triazines are possible as well. As noted previously, these intermediates have been shown to exist by derivatization or NMR spectroscopy.

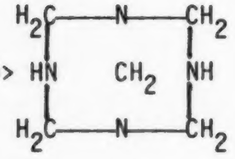
**VI + VII** <===>



(9)

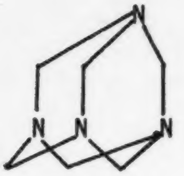
**VIII**

**VI + VIII** <===>



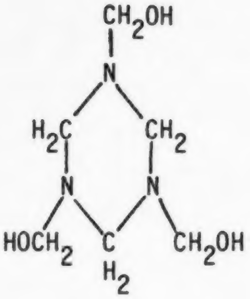
(10)

**IX**

**IX** + $CH_2O$ --->  (11)

**X**

Reactions 9 - 11 agree with the NMR spectrocopy observations. An alternative pathway that has been proposed for hexamine formation is 12-13. Ogata and Kawasaki (19) consider this implausible because all the methylol groups would have to be in the cis-configuration. Reaction 11 does not have this hindrance.

**VIII** + $3CH_2O$ --->  (12)

**XI**

**XI** + NH3 ---> **X** (13)

The production of formic acid via 14 or 15 has been postulated (22, 26).

$$\textbf{IV} + CH_2O \text{ ---> } CH_3NH_2 + HCOOH \qquad (14)$$

$$CH_2(OH)_2 + {}^{+}CH_2NH_2 \text{ ---> } HCOOH + CH_3NH_3 + H^{+} \qquad (15)$$

Subbaiah et al. (26) based their proposal that formic acid was a product of aldehyde ammonia reaction on acidity measured by titration. Reaction 4 followed be 5 or 8a,b is a more plausible source for the acidity they measured; this does not resort to the unlikely reaction given in 15.

## DISCUSSION

The kinetics of hexamine and triazine formation from $CH_2O$ and $NH_3$ do not appear to be rapid enough to be of environmental significance. Furthermore, the large exponents on the reactants in the equilibrium expressions causes the stability of product to be low when the reactants are at millimolar concentrations. However, some very rapid reaction rates for carbinolamine formation from higher aldehydes and amines have been observed; the equilibria for these complexes are moderately favorable as well. The pH dependence of $NH_3$ concentration will act to reduce the formation rate and stability of these products, however, so they may only be important near the $pK_a$ of ammonia.

The potential for production of acidity by $CH_2O$-$NH_3$ reactions is especially significant for the environmental application of this reaction. If the rate of reaction is appreciable at moderate pH, acidity would be produced by complexation of $NH_3$ and release of the proton. Subbaiah et al. (26) reported rapid generation of acidity, but they were working at elevated temperature and concentration. This behavior needs to be verified at environmental temperatures and concentrations by adding $CH_2O$ to an ammonium salt at neutral to moderately acidic pH and monitoring the pH.

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## Table 1

## Kinetic Data for $CH_2O + NH_3$

$$\nu = k\,[CH_2O]^2[NH_3]$$

| k ($\underline{M}^{-2}$ sec$^{-1}$) | $E_a$ (kcal/mole) | T (K) | pH | reference |
|---|---|---|---|---|
| $1\text{-}3 \times 10^{-3}$ | -- | 273 | unbuffered | 3 |
| $1.9\text{-}3 \times 10^{-3}$ | 17.1 | 288-293 | unbuffered | 4 |
| 25.2 | -- | 293 | 9.8 | 14,19 |
| 0.04 | -- | 293 | 6.3 | 14,19 |
| 0.58 | -- | 293 | 10.5-10.2 * | 14,19 |
| 0.56 | $k=1.13 \times 10^9 e^{(-14200/RT)}$ | 273-333 | unbuffered | 28 |

* unbuffered

## Table 2

## Equilibria in Aldehyde-Ammonia Reaction

| Equilibria | K | ΔH (kcal mole$^{-1}$) | Temperature (K) | Reference |
|---|---|---|---|---|
| $\frac{[(CH2)_6N_4][H^+]^4}{[CH_2O]^6[NH4]^4}$ | $6.3 \times 10^{-11}\ \underline{M}^{-5}$ | 19.48 | varied | 3 |
| $\frac{[(CH_3CHNH)_3]}{[CH_3CHO]^3[NH_3]^3}$ | $2 \pm .6 \times 10^{9}\ \underline{M}^{-5}$ | | 283 | 10 |
| $\frac{[CH_3CH(OH)NH_2]}{[CH_3CHO][NH_3]}$ | $2 < K > 17\ \underline{M}^{-1}$ | | 283 | 10 |
| $\frac{[CH_3CH(OH)NH_2]}{[CH_3CHO]([NH_3]-[A^-])}$ | $46.3\ \underline{M}^{-1}$ | | 293 | 20 |
| $\frac{[C_2H_5CH(OH)NH_2]}{[C_2H_5CHO]([NH_3]-[A^-])}$ | $10.5\ \underline{M}^{-1}$ | | 283 | 21 |
| $\frac{[C_3H_7CH(OH)NH_2]}{[C_3H_7CHO]([NH_3-[A^-])}$ | $7.9\ \underline{M}^{-1}$ | | 283 | 21 |
| $\frac{[C]}{[P][A]}$ [1] | 50 | | 298 | 6 |
| $\frac{[CH^+]}{[P][AH^+]}$ | 13 | | 298 | 6 |
| $\frac{[IM]}{[RCHO][RNH_2]}$ [2] | ≈100 | | 308 | 9 |
| $\frac{[C]}{[RCHO][RNH_2]}$ | 5 - 9 | | 308 | 9 |

## Table 2 (cont.)

## Equilibria in Aldehyde-Ammonia Reaction

| Equilibria | K | ΔH (kcal $mole^{-1}$) | Temperature (K) | Reference |
|---|---|---|---|---|
| $\frac{[C]}{[CH_2O][RNH_2]}$ | $10^4 - 10^6$ 3 | | 293-298 | 24 |

1) C = Carbinolamine, A = piperazine, P = pyridine-4-aldehyde

2) IM = Imine, R = Me or n-Pr

3) $RNH_2$ = urea, amino acids, methyl- and ethylamine

## Table 3

### Kinetics of Aldehyde Amine Reactions

$RCHO + R'NH_2 \text{ ---> } RCH(OH)NHR$

| R | R' | $k_f$ ($\underline{M}^{-1}$ $s^{-1}$) | $k_r$ ($s^{-1}$) | pH | T (K) | Reference |
|---|---|---|---|---|---|---|
| $CH_3$ | H | $> 1 \times 10^4$ | > 300 | 7.0 | 283 | 10 |
| $CH_3$ | H | [1] $2.93 \times 10^{-2}$ | $3 \times 10^{-3}$ | 9.74-8.93 | 293 | 20, 21 |
| $C_2H_5$ | H | [1] $2.1 \times 10^{-2}$ | $4 \times 10^{-3}$ | 10.4-9.3 | 293 | 21 |
| $C_3H_7$ | H | [1] $2.3 \times 10^{-2}$ | $4.4 \times 10^{-3}$ | 10.4-9.3 | 293 | 21 |
| p[2] | piperazine | $2\text{-}3 \times 10^5$ | $4\text{-}6 \times 10^3$ | varied | 298 | 6 |
| i-Pr | Me | 53 | --- | ≈ 10.3 | 308 | 9 |
| i-Pr | n-Pr | 50 | --- | ≈ 10.2 | 308 | 9 |

1) May be rate for formation of triazine

2) Pyridine-4-aldehyde